1,4 MIGRATION OF THE p-BIPHENYLYL GROUP IN THE REACTIONS OF 4-CHLORO-1-p-BIPHENYLYL-1,1-DIPHENYLBUTANE WITH ALKALI METALS

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Approved:

Chairman

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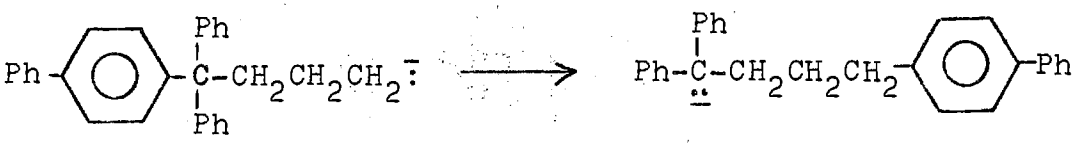
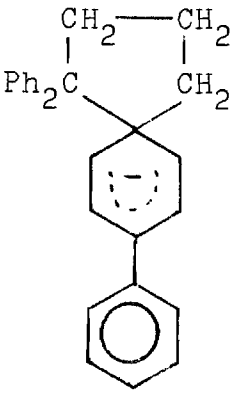
SUMMARY

The purpose of this research was to study the products from the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with various alkali metals to determine if a rearrangement of the carbon skeleton involving 1,4 migration of the p-biphenylyl group occurs in the carbanion I to give II:



I II

Rearrangements of organoalkali compounds involving 1,2 migration of aryl groups are well documented, whereas 1,4 migration of the phenyl group occurs only as a minor process in the reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals. In the present work the chloride (1) was chosen since the p-phenyl group should help to stabilize the intermediate III for 1,4 migration of p-biphenylyl as exemplified by contributions of structures such as IV to the hybrid structure of the anion III.



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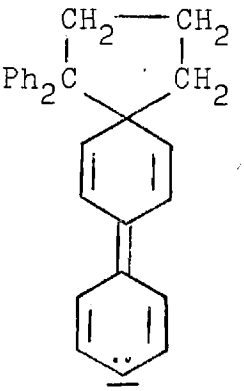
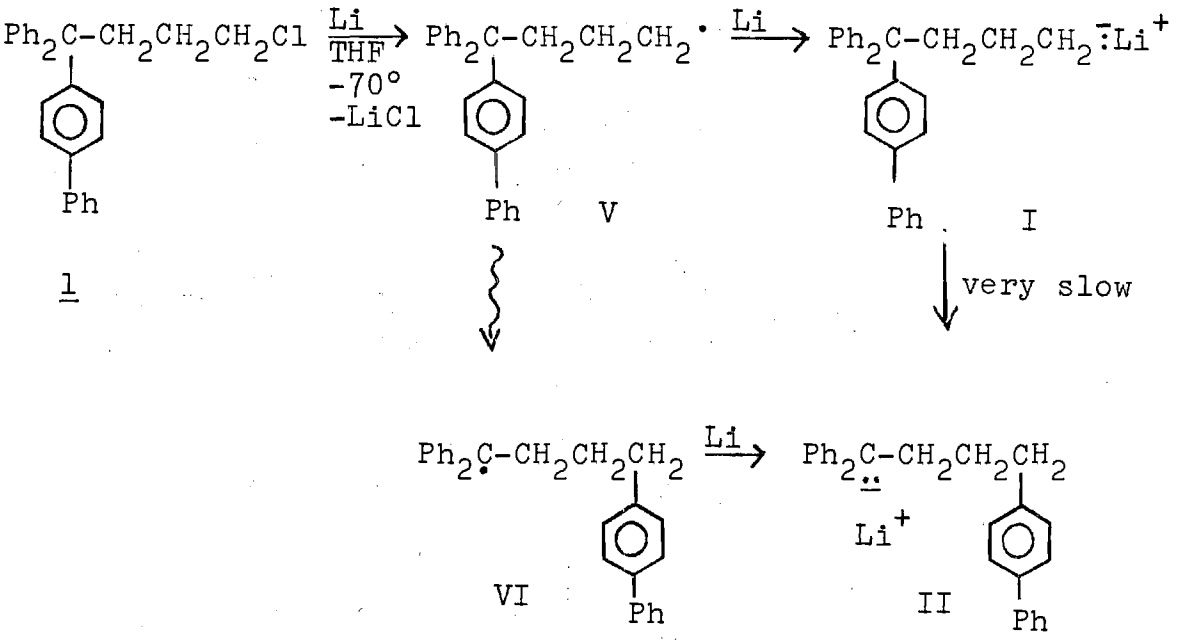


IV

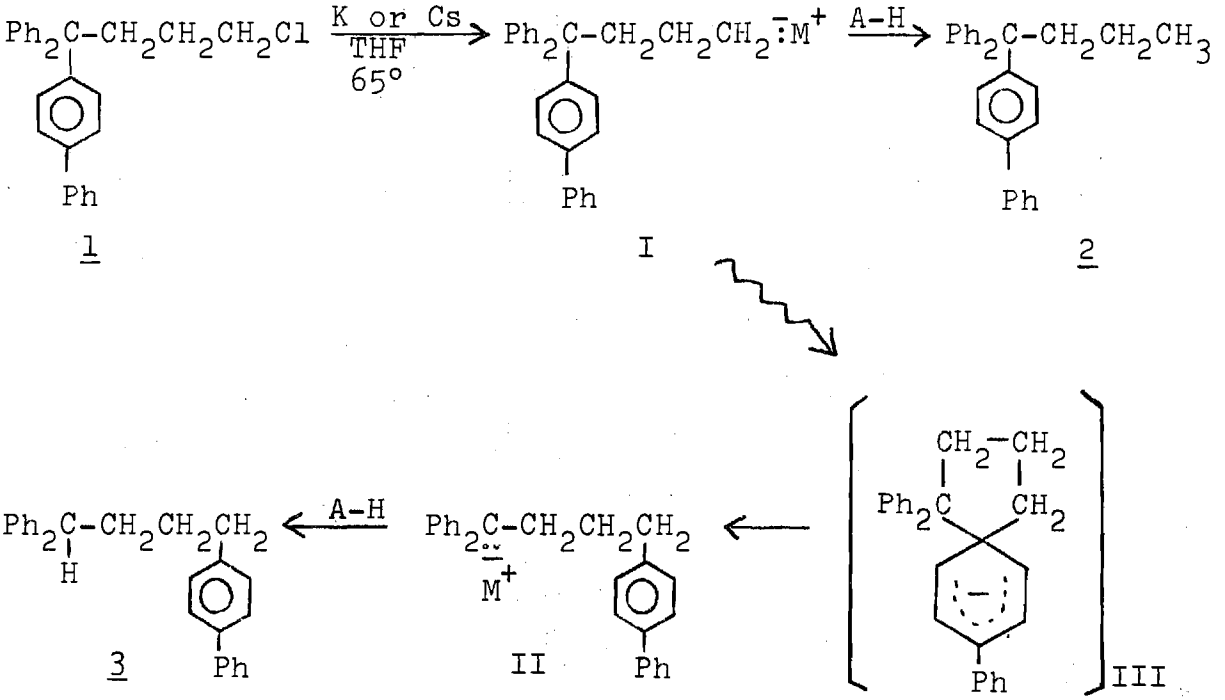
The chloride (1), mp 99 - 100°, was prepared by reaction of p-biphenylyldiphenylmethylsodium with excess of 1-bromo-3-chloropropane. Reaction of the chloride (1) with lithium metal in THF at -70° gave upon hydrolysis a 76 to 24 ratio of 1-p-biphenylyl-1,1-diphenylbutane (2) to 4-p-biphenylyl-1,1-diphenylbutane (3); upon standing for 4 hours at 0°, the solution gave 69 to 31 ratio of unrearranged to rearranged products. Since 24% rearrangement took place during the reaction with lithium at -70° but only about 7% more rearranged at 0°, it is concluded that 4-p-biphenylyl-4,4-diphenylbutyllithium rearranges very slowly even at 0°; therefore, the large quantity of rearrangement at -70° must be via another process -- it is suggested that this rearrangement is via an intermediate radical V formed at or near the surface of the lithium metal (see Scheme I).

Scheme I



Reaction of the chloride (1) with finely divided potassium metal (in a Morton high-speed stirring apparatus) in boiling THF gave a dark red solution which upon carbonation yielded 5-p-biphenylyl-2,2-diphenylpentanoic acid, mp 191 - 192°, or upon decomposition with methanol gave 3, mp 81 - 82°, containing only some 1% of 2, mp 94.5 - 95°. Reaction of the chloride (1) with finely divided cesium over a period of 4 minutes in boiling THF gave the same rearranged carbanion according to analysis of the products from carbonation and protonation. These results may be explaned by the following Scheme II.

Scheme II



In view of the fact that phenyl groups are known to undergo 1,4 migration in free radicals, to establish Scheme II it is necessary to show that formation of carbanion I precedes rearrangement of the p-biphenylyl group. In experiments designed to trap the intermediate anion I, the chloride (1) was allowed to react at 65° in THF with increments of potassium and t-butyl alcohol, the latter always in slight excess. Analysis of the reaction mixture at intervals revealed that 1-p-biphenylyl-1,1-diphenylbutane (2) was an initial product of the reaction. The maximum yield of 2 was 18% but this product largely disappeared with continued reduction by excess potassium. The final product consisted of 3% of 2, 90% of

1-(p-cyclohexylphenyl)-1,1-diphenylbutane (4), mp 100.5 - 102° and 6% of an unknown (5). Compound 5 is evidently a 1,4-dihydro derivative of 2 since (unlike 4 which was unaffected) it gave 2 upon treatment with 5% Pd-C at 100°. The structure of 4 was confirmed by its mass spectrum (peaks at m/e 368 and 325) and nmr spectrum. Since alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from t-butyl alcohol, the intermediate trapped by addition of small amounts of t-butyl alcohol, in the present experiments must be the carbanion I, as shown in Scheme II, rather than the corresponding free radical.

Reaction of the chloride (1) with potassium in the more acidic solvent dioxane at 101°, rather than THF at 65°, gave the rearranged hydrocarbon 3 (75% yield) and no detectable 2 and reaction of the chloride (1) with cesium in dioxane at 30° to 40° gave initially chiefly the rearranged hydrocarbon 3, which underwent further reduction to 4-(p-cyclohexylphenyl)-1,1-diphenylbutane and the cleavage product of 4-(p-cyclohexylphenyl)-1-phenylbutane. However, reaction of the chloride (1) with sodium in dioxane at 101° gave an 8 to 92 ratio of rearranged to unrearranged hydrocarbon (3:2). These reactions in the solvent dioxane confirm the conclusion derived from work in THF and show moreover that the rate of rearrangement of the organopotassium and cesium compounds (I)

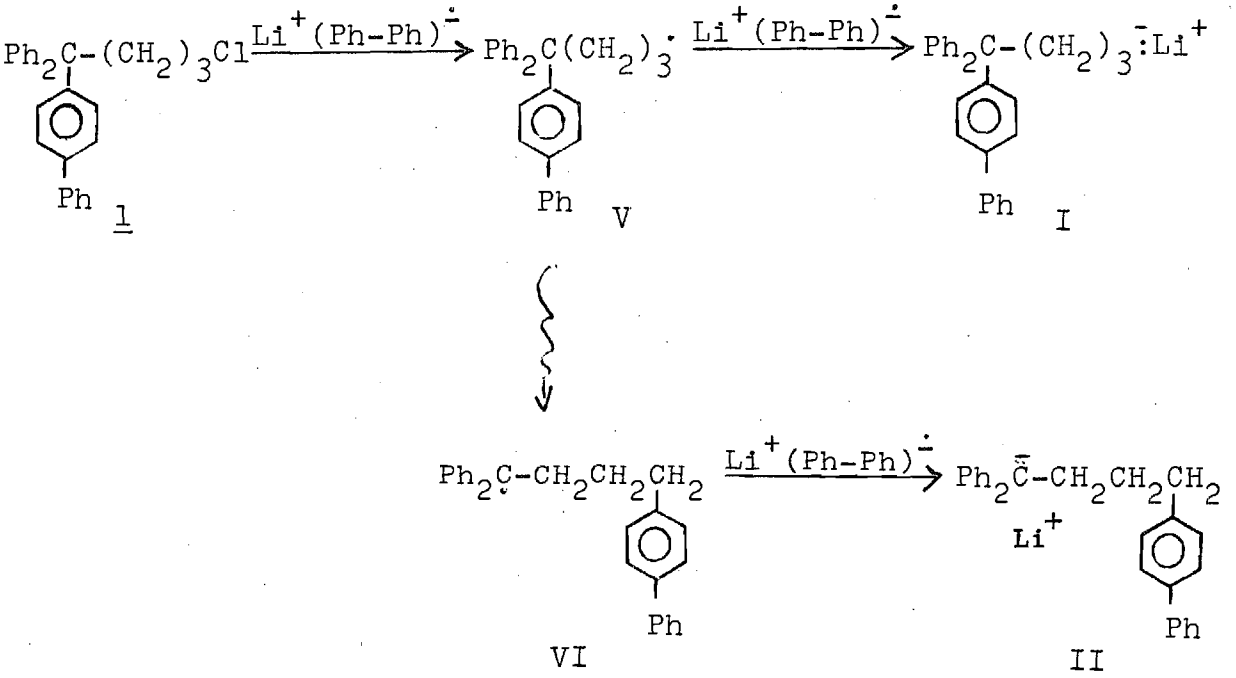
greatly exceeds that of the corresponding organosodium compound. The inequality of rate between sodium and potassium or cesium compounds in carbanion rearrangements has not been previously observed although it has been known for some time that organolithium compounds rearrange more slowly than organosodium or organopotassium compounds.

According to Scheme II the spiro anion III is an intermediate in the present carbanion rearrangement. In an attempt to detect this intermediate the chloride (1) was allowed to react with excess finely divided Cs-K-Na alloy in THF at -75° for some three minutes before carbonation. There was obtained on carbonation, however, only the usual product of rearrangement, 5-p-biphenylyl-2,2-diphenylpentanoic acid. This result implies that the spiro anion III rearranges readily to II even at -75°. Ready ring opening of this spiro anion III may be dependent upon the presence of the two phenyl groups which stabilize the final anion II. The observed chemical shifts of the aromatic protons in the nmr spectrum (at room temperature) of the carbanion solution from the reaction of the chloride (1) with Cs-K-Na alloy in THF at -75° confirms the structure of the product as an anion II rather than spiro anion III.

Reaction of the chloride (1) with excess lithium biphenyl in THF at -75° gave upon protonation with methanol a 98 to 2 ratio of unrearranged to rearranged hydrocarbon (2:3); or upon carbonation a 97 to 3 ratio of 1-p-biphenylyl-1,1-diphenylpentanoic acid (55% yield) to 5-p-biphenylyl-2,2-di-

phenylpentanoic acid.

Scheme III



The reaction products here showed less rearrangement than the products from direct reaction of the chloride (1) with lithium metal, moreover, the amount of rearrangement decreased with increasing concentration of lithium biphenyl. The interpretation is that the intermediate radical V is "trapped" by reaction with a second molecule of lithium biphenyl before it can rearrange appreciably to VI (see Scheme III).

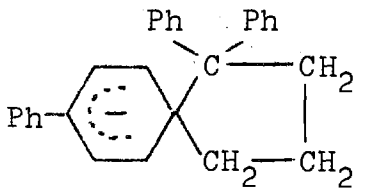
Addition of excess potassium t-butoxide to a solution of 4-p-biphenylyl-4,4-diphenylbutyllithium (I) in THF at -75° resulted within 10 minutes in complete disappearance of organolithium compound (I) and appearance of rearranged organo-

alkali compound (II) as shown by products of carbonation and protonation. This process of catalysis of rearrangement of an organolithium compound by potassium t-butoxide (a Lewis base) is somewhat analogous to catalysis of Wagner-Meerwein rearrangements of alkyl halides by aluminum chloride (a Lewis acid). In the former case the potassium t-butoxide gives rise to a nearly "free" carbanion, while in the latter case aluminum chloride gives a nearly "free" carbonium ion; both then rearrange. Potassium t-butoxide has previously been reported to activate butyllithium toward metalation of hydrocarbons such as toluene and benzene.

CHAPTER I

INTRODUCTION

The objective of this research[1] was to explore the products from the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with various alkali metals to determine if rearrangement of the carbon skeleton involving 1,4 migration of the p-biphenylyl group occurs in the carbanion. This halide was chosen since the p-phenyl group should help to stabilize the intermediate spiro anion III for 1,4 migration of p-biphenylyl relative to intermediate XI for ortho-cyclization.



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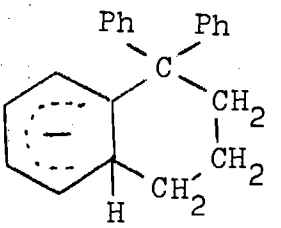

XI

Carbanions (organometallic compounds) are frequently used as reagents in organic synthesis. It is commonly assumed that the structures of the products from such syntheses can be inferred from those of the starting materials; however, some

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1. A portion of this research has been published; see E. Grovenstein, Jr., S. Akabori, and Jung-Ung Rhee, J. Amer. Chem. Soc., 94, 4734 (1972).

years ago Grovenstein[2] and independently, Zimmerman and Smentowski[3] discovered the rearrangement of 2,2,2-triphenylethylsodium to 1,1,2-triphenylethylsodium in ethereal solvents. Moreover, 2,2,2-triphenylethylsodium and -potassium have been found to rearrange much more readily than 2,2,2-triphenylethyllithium.[4a] Phenyl groups have also been found to undergo 1,2 migration in 2,2-diphenylpropyllithium and -potassium and in 2-phenyl-2-(p-tolyl)propyllithium (wherein preferential phenyl over p-tolyl migration was observed).[5] A benzyl group has been found to undergo 1,2 migration in 2,2,3-triphenylpropyllithium,[4b] in which the migration of benzyl occurs via an elimination-readdition of benzyl group presumably as the benzyl anion.[6a] A 1,2 migration of p-biphenylyl (in preference to m-biphenylyl) has been observed in 1-m-biphenylyl-1,1-bis(p-biphenylyl)ethyllithium.[6c] In all these cases the organoalkali compound formed upon rearrangement is thermodynamically more stable than the original organoalkali compound, e.g.,

$$Ph_3CCH_2Li \xrightarrow{\sim Ph} (Ph_2\ddot{C}CH_2Ph)Li^+$$

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2. E. Grovenstein, Jr., ibid., 79, 4985 (1957).

3. H. E. Zimmerman and F. J. Smentowski, ibid., 79, 5455 (1957).

4. (a) E. Grovenstein, Jr. and L. P. Williams, Jr., ibid., 83, 412 (1961); (b) ibid., 83, 2537 (1961).

5. H. E. Zimmerman and A. Zeig, ibid., 83, 1196 (1961).

6. (a) E. Grovenstein, Jr. and G. Wentworth, ibid., 85, 3305 (1963); (b) ibid., 89, 1852 (1967); (c) ibid., 89, 2348 (1967).

where 1,1,2-triphenylethyllithium unlike 2,2-triphenylethyllithium is a resonance-stabilized anion with a delocalized charge.

Grovenstein and Cheng[7] have recently reported that reaction of 1-chloro-2-p-biphenylethane-1,1-d_2 with excess lithium metal in THF at -70° gave a good yield of 2-p-biphenyllithium-1,1-d_2, which did not undergo appreciable rearrangement on warming to 0° as judged by the position of the deuterium label in the products of carbonation and protonation. In contrast, reaction of the same chloride with cesium or potassium metal in THF at reflux temperature gave essentially a 50/50 mixture of 1-p-biphenylylethane-2,2-d_2 and 1-p-biphenylethane-1,1-d_2; in the reaction of the chloride at -65° with Cs-K-Na alloy, scrambling of the label in the p-biphenylylethane was only partial; repetition of the reaction with potassium in the presence of a small amount of t-butyl alcohol resulted in a greatly reduced amount of rearrangement in the product p-biphenylylethane. Since formation of 2-p-biphenylylethyl anion preceded appreciable rearrangement, they found no evidence for participation of p-biphenylyl radical anion (or dianion) as a powerful nucleophile which displaced chloride to give directly the spiro radical (or corresponding anion).

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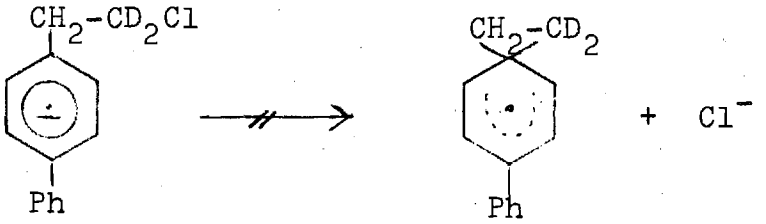
7. E. Grovenstein, Jr. and Y. M. Cheng, ibid., 94, 4971 (1972).



Their failure to observe direct participation of neighboring p-biphenylyl in a concerted reductive rearrangement of the chloride is in accord with the accepted mechanism[8] for the intermolecular reaction of naphthalene radical anion with alkyl halides wherein the first step gives naphthalene and a free alkyl radical rather than an alkylnaphthalene derivative (the latter is formed only in a subsequent step).

They[9] also have reported that reaction of 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) with lithium metal in THF at -65° gave, according to the results of carbonation, 2-methyl-2-phenylpropyllithium containing 6.4% of 1,1-dimethyl-2-phenylethyllithium (product of 1,2-phenyl migration). Since warming their reaction mixture to 4° gave chiefly the corresponding hydrocarbons but failed to give additional products of phenyl migration, the results indicated that the organolithium compound from neophyl chloride does not rearrange to 1,1-dimethyl-2-phenylethyllithium. Therefore, they suggested that

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8. For a recent review see N. L. Holy and J. D. Marcum, Angew. Chem., Int. Ed. Engl., 10, 115 (1971).

9. E. Grovenstein, Jr., and Y. M. Cheng, Chem. Commun., 101 (1970).

the observed rearrangement took place in an intermediate, presumably the neophyl radical, prior to formation of the organolithium reagent. Thus, here and in the work of Cram and Dalton,[10] rearrangements of radicals or radical anions and not rearrangements of organoalkali compounds evidently accounts for the small amount of phenyl migration observed.

Rearrangements of organoalkali compounds involving 1,2 migration of aryl groups are thus now well documented,[2-6] whereas 1,4 migration of the phenyl group occurs only as a minor process in the reaction[11] of 4-chloro-1,1,1-triphenylbutane with cesium and potassium. Reaction of this chloride with lithium at -60° in THF, however, gave the expected 4,4,4-triphenylbutyllithium which was not appreciably rearranged at temperatures up to 25° and time so long that only 4% of the organolithium reagent survived. In contrast, reaction of this chloride with potassium at reflux temperature in THF, followed by carbonation, gave some 75% yield of 1,1-diphenyl-1,2,3,4-tetrahydronaphthalene. Evidently at 65° 4,4,4-triphenylbutylpotassium gives tetrahydronaphthalene via hydride elimination from the ortho-cyclization product a faster than it gives 1,1,4-triphenylbutyl anion via 1,4 phenyl migration;

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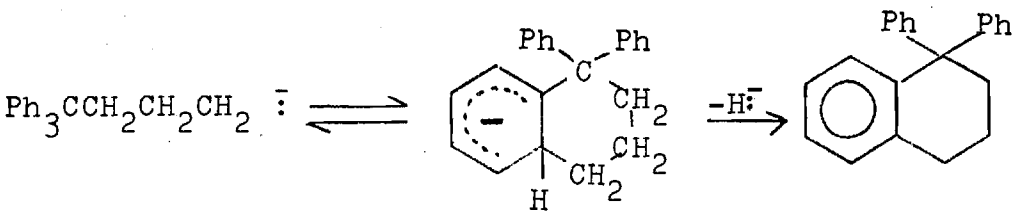
10. D. J. Cram and C. K. Dalton, J. Amer. Chem. Soc., 85, 1268 (1963).

11. E. Grovenstein, Jr., J. A. Beres, Y. M. Cheng, J. A. Pegolotti, J. Org. Chem., 37, 1281 (1972).



a

Reaction of the same chloride with cesium-potassium alloy at -45° in THF followed by addition of methanol, gave some 10% yield of 1,1,4-triphenylbutane (product of 1,4 phenyl migration) but the major products were 9-phenyl-n-propyl-fluorene and hydroderivatives.[11]

Julia and Malassine[12] have recently reported that reaction of 4-chloro-n-butyl-p-benzoic acid with lithium in liquid NH_3 gave 60% of spiro [4.5] deca-6,9-diene-8-carboxylic acid and 38% of n-butyl-p-(1,4-dihydro)benzoic acid; in the presence of ethyl alcohol the reaction gave the same products in the same yield. Reaction of the corresponding bromo and iodo acids under the same reaction conditions gave increased yields of n-butyl-p-(1,4-dihydro)benzoic acid (e.g., 81% with X = Br; 85% with X = I) and 4-n-butylbenzoic acid (e.g., 12% with X = Br; 15% with X = I) while the yield of spiro [4.5] deca-6,9-diene-8-carboxylic acid was decreased (e.g., 7% with X = Br; 0% with X = I).

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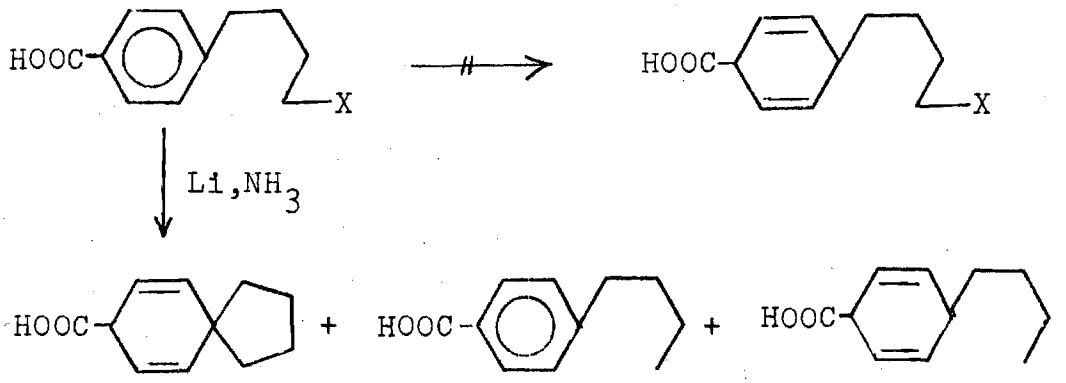
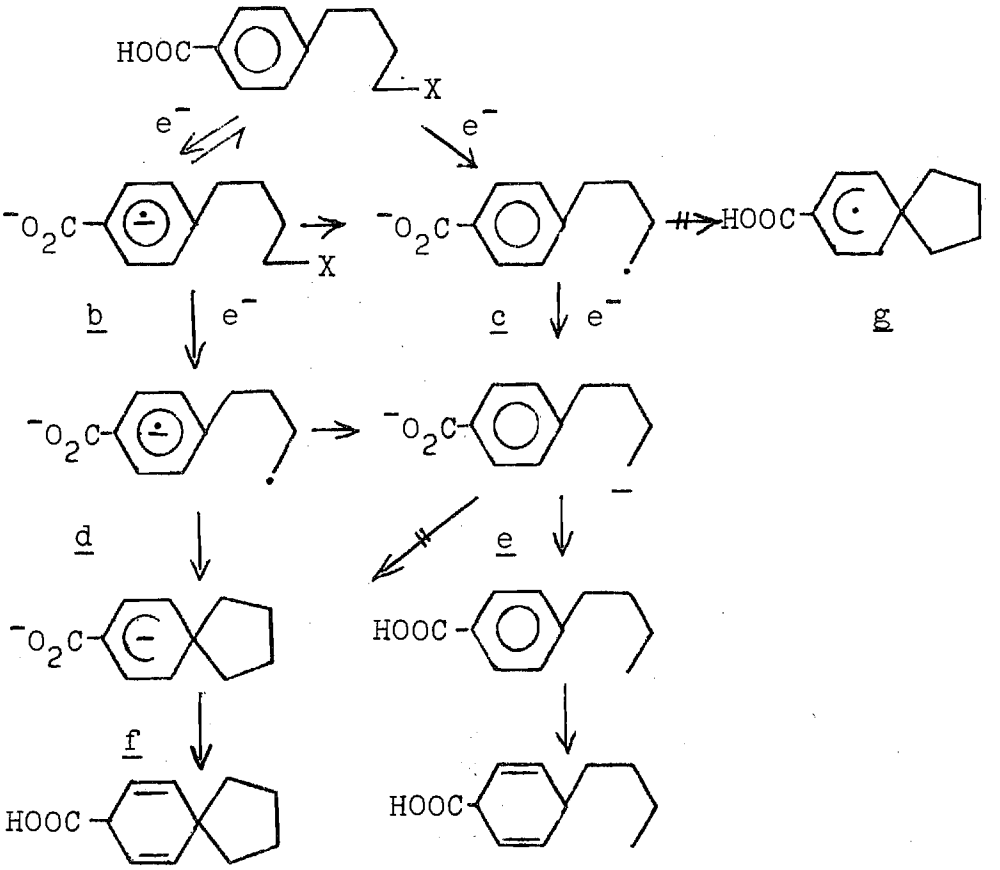
12. M. Julia and B. Malassine, Tetrahedron Lett., No. 24, 2495 (1972).



Julia and Malassine further reported that the yield of spiro [4,5] deca-6,9-diene-8-carboxylic acid from the reaction of 4-chloro-n-butyl-p-benzoic acid with lithium increased from 60 to 70% upon going from liquid ammonia to a 1 to 5 mixture of ammonia and tetrahydrofuran as solvent; in contrast, the yield of the spiro acid decreased to 37% when the chloro acid was reacted with sodium in place of lithium in liquid ammonia under the same reaction conditions and to only 27% yield with potassium. They proposed the following mechanism to account for their results (see Scheme IV).

Scheme IV

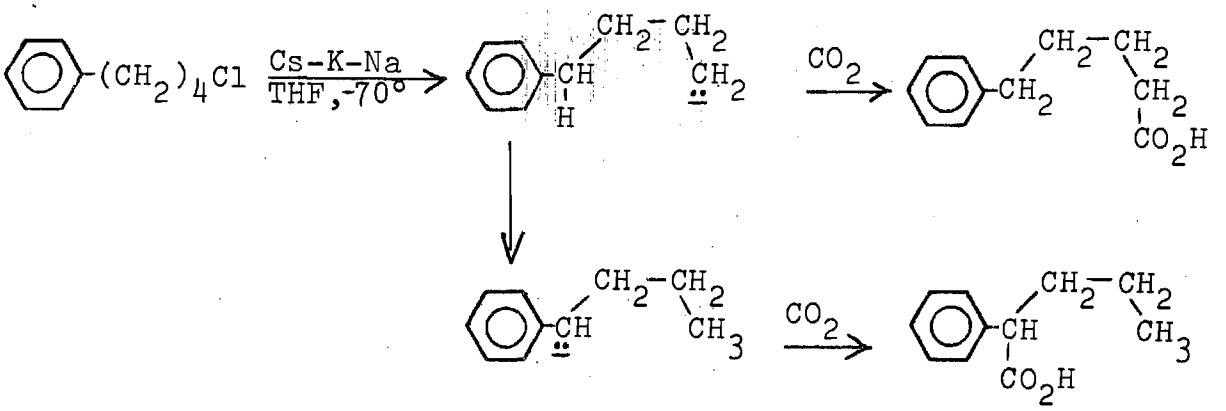


Since spiro [4,5] deca-6,9-diene-8-carboxylic acid was not obtained from the reaction of 4-iodo-n-butyl-p-benzoic acid with lithium in liquid ammonia it seems to be obvious that the dianion e does not cyclize to corresponding spiro dianion f and for the same reason that the radical anion c does not cyclize to the corresponding radical anion g.

Similarly, it was found that 4-phenylbutyl anion[13] failed to cyclize in appreciable yield to spiro [4,5] deca-6,9-

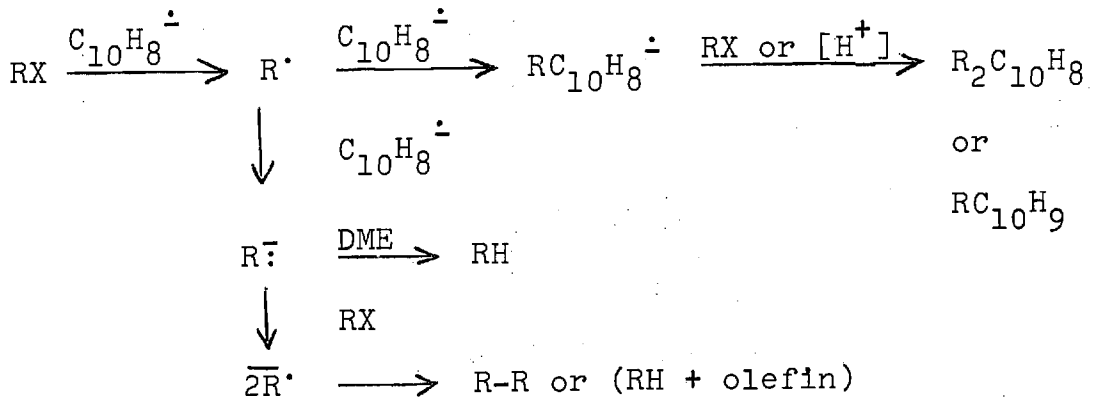
13. Unpublished work of E. Grovenstein, Jr. and S. Akabori, Georgia Institute of Technology.

dienyl anion in the reaction of 1-chloro-4-phenylbutane with excess Cs-K-Na alloy at -70° in THF since the carbonation product contained 86% yield of 2-phenyl-1-pentanoic acid, 2.5% of 4-phenyl-1-pentanoic acid, and small quantities of three unknowns. Thus, in sharp contrast to 4-p-biphenylylbutyl anion[1] which primarily undergoes cyclization to 8-phenylspiro [4,5] deca-6,9-dienyl anion in the reaction of 4-chloro-1-p-biphenylylbutane with excess Cs-K-Na alloy at -70° in THF, the 4-phenylbutyl anion undergoes what appears to be a 1,4 migration of hydrogen;



While in the present work organoalkali compounds of the 4-p-biphenylyl-4,4-diphenylbutyl system were generally prepared by direct reaction of the corresponding chloride with the appropriate alkali metal, organolithium compounds were also prepared by reaction of lithium biphenyl upon 4-chloro-1-p-biphenylyl-1,1-diphenylbutane. In related work reaction of sodium naphthalene with alkyl halides in 1,2-dimethoxy-

ethane has been found to lead to reduction[14,15] alkylation[16,17] and dimerization products.[14] Since the distribution of the reaction products depends strongly on the nature of the halogen involved and somewhat on the nature of the alkyl group and reaction conditions, Garst[18] has been led to suggest the following mechanism for these reactions:



In the mechanism the initial step is an electron-transfer reaction which produces an alkyl radical, and is immediately

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14. G. D. Sargent, J. N. Cron, and S. Bank, J. Amer. Chem. Soc., 88, 5363 (1966).

15. (a) J. F. Garst, P. W. Ayers, and R. C. Lamb, ibid., 88, 4260 (1966); (b) Preprints, Meeting, Amer. Chem. Soc., Div. Petrol. Chem., 13, D65 (1968); (c) J. F. Garst and F. E. Barton, Tetrahedron Lett. 587 (1969).

16. (a) D. Lipkin, F. R. Galiano, and R. W. Jordan, Chem. Ind. (London) 1963, 1957; (b) D. Lipkin, G. J. Davis, and R. W. Jordan, Preprints, Meeting, Amer. Chem. Soc., Div. Petrol. Chem., 13, D61 (1968).

17. N. D. Scott and J. F. Walker, U. S. Patent 2150039 (1939).

18. J. F. Garst, Accounts of Chem. Res., 5, 400 (1971).

followed by competitive reactions, which invoke sodium naphthalene as a scavenger for the initially formed alkyl radicals. Alkyl radicals either combine with sodium naphthalene or are reduced by it to intermediate alkyl anions. An experimental fact supporting alkyl anion intermediates has been found in the reaction of sodium naphthalene with alkyl halides in THF to Grignard reagents.[19] This result can be interpreted as the trapping of intermediate alkyl sodium by $MgBr_2$;

$$R^{-}Na^{+} \xrightarrow{MgBr_2} RMgBr + NaBr$$

Other direct evidence for an intermediate alkyl anion was found in the reaction of lithium naphthalene with 5-hexenyl chloride involving the reaction mixture after treatment with D_2O gave 1-hexene and methylcyclopentane which were both about 35% monodeuterated.[20]

In the present work 4-p-biphenylyl-4,4-diphenylbutyllithium was reacted with an excess of potassium t-butoxide in THF to give what can be most simply regarded as the corresponding organopotassium compound.

It has been reported[21] that organolithium compounds

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19. S. Bank and J. F. Bank, Tetrahedron Lett., 4533 (1969).

20. J. T. Barbas and J. F. Garst, unpublished observations.

21. L. Lochmann, J. Pospisil, and D. Lim, Tetrahedron Lett., 257 (1966).

containing normal alkyl groups react with sodium t-butoxide in heptane to give a good yield of the corresponding organosodium compound as an insoluble precipitate in high degree of purity. Similarly some organopotassium compounds have been prepared as insoluble precipitates in good yield and relatively pure by treatment of organolithium compounds in cyclohexane or heptane as solvent with potassium (-) (IR)-menthoxide.[22] In other cases treatment of potassium t-butoxide with an excess of n-butyllithium in heptane has been found to form a n-butylpotassium-n-butyllithium adduct[21] (this type of addition compound has been assumed to exist by Bryce-Smith,[23] who reacted metallic potassium with n-butyllithium in benzene).

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22. L. Lochmann and D. Lim, J. Organometal. Chem., 28, 153 (1971).

23. (a) D. Bryce-Smith, J. Chem. Soc., 861 (1953); (b) ibid., 5983 (1963).

CHAPTER II

REAGENTS AND SOLVENTS

Acetic Acid, Glacial

Baker reagent grade glacial acetic acid was used without further purification.

Acetone

Commercial grade acetone was redistilled at 56° from potassium permanganate.

Ammonium Chloride

Baker reagent ammonium chloride was used without further purification.

Acetyl Chloride

Baker reagent grade acetyl chloride was redistilled at 54° from dimethylaniline.

Benzene

Matheson, Coleman & Bell, Inc., industrial grade (thiophene free) benzene was stored over sodium wire.

Benzophenone

Eastman white label grade benzophenone was used without further purification.

Biphenyl

Eastman white label grade biphenyl was used without further purification.

Bromobenzene

Unmarked brown-bottled bromobenzene (recorded bp. 154.5 — 155°, student preparation) from the organic stockroom of Georgia Institute of Technology was redistilled at 150° through a 70 cm-Vigreux column.

1-Bromo-3-Chloropropane

Eastman white label grade 1-bromo-3-chloropropane was redistilled at 141 — 142° through a 60 cm vacuum jacketed column packed with glass helices.

p-Bromobiphenyl

Eastman white label grade p-bromobiphenyl was recrystallized (mp. 89.5 — 90°) from ethanol following treatment of the ethanolic solution with zinc dust and conc. HCl.[24]

Bromodiphenylmethane

Aldrich Chemical Co., Inc. reagent grade bromodiphenylmethane was purified to colorless crystalline product (mp. 38-40°) by vacuum distillation (bp. 156-157°) at 10 mm Hg.[25]

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24. M. Gomberg and W. E. Backman, Org. Syntheses, Collective Volume I, John Wiley & Sons, Inc., New York, 1948, p. 113.

25. N. H. Cromwell and W. E. Fettzgibbon, J. Amer. Chem. Soc., 70, 389 (1948).

1-Bromopropane

Eastman white label grade 1-bromopropane was redistilled at 70.5° through a 60 cm vacuum jacketed column packed with glass helices.

t-Butyl Alcohol

Baker reagent grade t-butyl alcohol was redistilled from over molten potassium at 81° through a 60 cm vacuum jacketed column packed with glass helices.

n-Butyllithium

Foote Mineral company n-butyllithium in pentane (conc. 12.91 %, Density 0.65 g/cc at 25°) was used without further purification.

Carbon Tetrachloride

Baker reagent grade carbon tetrachloride was used without further purification.

Cesium

MSA Research Corp., 99.9 percent minimum purity cesium was used without further purification.

1-Chloro-2-methyl-2-phenylpropane

A sample prepared by L. P. Williams, Jr.[26] was redistilled at 101° under 15 mm pressure through a 30 cm Vigreux column.

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26. L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, p. 56 (1962).

Cyclohexane

Phillips Petroleum Co., 99.5% minimum wt. % cyclohexane was used without further purification.

Diethylene Gylcol

Fisher Scientific Company purified grade diethylene glycol was used without further purification.

Diethyl Ether

Baker reagent grade anhydrous ether, stored over sodium wire, was used without further purification.

Dimethyl Sulfoxide

Matheson, Coleman & Bell, Inc., reagent grade dimethyl sulfoxide was used without further purification.

Dioxane

Fisher Scientific Company certified grade dioxane was purified according to the general procedure of Fieser.[27]

Ethyl Alcohol

Commercial grade absolute ethyl alcohol was used without further purification.

n-Heptane

Phillips Petroleum Co., pure grade n-heptane (99 mol %

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27. L. E. Fieser, "Experiments in Organic Chemistry" 3rd. Ed., D. C. Heath and Company, Boston, 1955, p. 285.

minimum) was stored over sodium wire.

n-Hexane

Phillips Petroleum Co., pure grade n-hexane (99 mole % minimum) was stored over sodium wire.

Ligroin

Commercial grade ligroin was stored over sodium wire.

Lithium

Lithium Corporation of America lithium wire containing 0.05 percent maximum sodium was used.

Lithium Aluminum Hydride

City Chemical Corp., 95 percent minimum, lithium aluminum hydride was used without further purification.

Magnesium

Eastman white label magnesium was used.

Methyl Alcohol

Matheson, Coleman & Bell, Inc., commercial grade methanol was redistilled at 64° from magnesium through a 30 cm Vigreux column.

Methyl Iodide

Eastman white label grade methyl iodide was used without further purification.

n-Pentane

Phillips Petroleum Co., pure grade n-pentane (99 percent minimum) was stored over sodium wire.

Potassium

Baker reagent grade potassium was used.

Potassium t-Butoxide

MSA Research Corp., potassium t-butoxide was used.

Sodium

Baker reagent grade sodium was used.

Sodium Aluminum Hydride

Metal Hydrides, Inc., pure grade of sodium aluminum hydride was used.

Sodium Cyanide

Baker analyzed grade sodium cyanide was used without further purification.

Tetrahydrofuran

Baker reagent grade tetrahydrofuran was stored over sodium wire.

CHAPTER III

GENERAL PROCEDURE FOR REACTIONS AND INSTRUMENTAL ANALYSES OF PRODUCTS

General Procedure

Reactions with alkali metals were normally conducted in a 500 ml Morton flask equipped with a Morton-high speed stirrer,[28] a condenser, a thermometer well, and a dropping funnel. The apparatus was flame dried under a stream of dry nitrogen. For reactions of cesium and Cs-K-Na alloy the entire apparatus were contained in a glove box under an atmosphere of nitrogen in order to reduce fire hazards in working with these readily oxidizable metals. Tetrahydrofuran (THF) was stored over sodium wire and freshly distilled into the reaction flask from lithium aluminum hydride or sodium aluminum hydride under a nitrogen atmosphere before use. When the reactions were conducted in dioxane as a solvent, the solvent was distilled into the flask from molten alkali metals (e.g., sodium or potassium) after the solvent was purified according to the general procedure of Fieser.[27] In some reactions of alkyl halides with lithium biphenyl or reactions of organolithium compound with potassium t-butoxide, two sets of the usual

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28. A. A. Morton and L. S. Redmon, Ind. Eng. Chem., 40, 1190 (1948).

apparatus were arranged side by side so that the reaction mixture could be siphoned from one flask into the other without being exposed to the atmosphere and the apparatus was kept under an atmosphere of nitrogen. In runs with liquid alkali metals, the solvent was stirred with the molten metal at reflux for normally 1 hr before addition of alkyl halide; this procedure ensured both that the solvent was freed of impurities and that the alkali metal was finely divided.

Instrumental Analysis

All nmr spectra were obtained on a Varian Associates Model A-60 Spectrometer using tetramethylsilane as an internal standard unless otherwise specified and carbon tetrachloride as solvent.

Mass spectral analysis were obtained either upon a Varian M-66 or Hitachi Perkin-Elmer RMU-7L Spectrometer and exact mass determination was made with the latter spectrometer.

Gas-chromatographic analysis of the reaction products were accomplished by using either Perkin-Elmer Model 881 (P-E) or F&M Research Chromatograph Model 810 (F&M). The column A and B in Perkin-Elmer 881 were 6 ft length, 1/8 inch outside diameter, packed with 5% Silicon Gum Rubber (SE-30) on 100-120 Mesh Chromosorb G-AW-DMCS (Chromosorb G, acid washed and treated with dimethyldichlorosilane). The columns in F&M 810 were 6 ft length, 1/4 inch outside diameter, packed with 10% Silicon Gum Rubber on 60-80 Mesh Chromosorb G-AW-DMCS and 6 ft length, 1/4 inch outside diameter, packed with 10% Apiezon L

on 60-80 Mesh Chromosorb G-AW-DMCS. Quantitative gas-chromatographic analyses of the reaction products were accomplished by making both product and authentic sample solutions of a known concentration by weighing and then injecting weighed amounts of each of those two solutions separately into the gas chromatograph machine under the same vpc conditions. The calculations are based on the assumption that the area to weight ratio of a compound in an unknown mixture is identical to the area to weight ratio of that same compound in an authentic sample solution. The yield of products were then expressed in weight ("absolute yield") or mol % yield based on the starting material used. If only the approximate relative compositions of the volatile products was determined, only vpc area percent was used ("relative yield").

CHAPTER IV

EXPERIMENTAL DETAILS

Synthesis of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane

p-Biphenylyldiphenylcarbinol

The titled carbinol was prepared following the procedure of Lichtin and Glazer.[29] In the first run, 3.23 g (0.465 g-atom) of Li wire which had been stored under mineral oil, was rubbed with a Kimwipe to ensure a bright surface, washed with petroleum ether (bp 60 - 70°), and cut into pieces 3 mm in length, was dispersed in 200 ml of ether dried over sodium wire and was added under a nitrogen atmosphere to a flame-dried three-necked 1-l Morton flask equipped with a high-speed stirrer, a water condenser and a dropping funnel. Then about 0.5 ml (0.0080 mole) of methyl iodide was added with moderate stirring to initiate reaction. After 10 minutes stirring, 50.3 g (0.216 mole) of purified p-bromobiphenyl[24] in 700 ml of dried ether was added dropwise over a one and one-half hour period. At the beginning of the addition, the reaction mixture turned black-brown and gradually changed to black. Then the solution was heated at reflux with high-speed stirring for 5 hours before aliquots of 5 ml

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29. N. N. Lichtin and H. Glazer, J. Amer. Chem. Soc., 73, 5537 (1951).

each of reaction mixture were withdrawn for Gilman titration;[30] from the titrations the yield of p-biphenylyllithium was calculated to be about 44%. To the rest of the reaction mixture, 17.6 g (0.0969 mole) of benzophenone in 100 ml of dried ether was added over a two hour period. The color of the solution changed to dark blue when the benzophenone was added. Then the solution was refluxed for an additional hour before it was treated with a solution of NH_4Cl containing cracked ice. After standing overnight at room temperature, yellow-colored reaction mixture was steam distilled for 12 hours to remove volatile impurities. During the steam distillation, yellow crystals began to form at the bottom of flask. The collected crude carbinol was purified by dissolving in an excess of petroleum ether (bp 90 - 110°). A yellow solid (mp 128 - 134°) precipitated on cooling the solution. The solid was separated by filtration and recrystalized several times from hot petroleum ether to give slightly yellow colored crystals (mp 132 - 137°). These were recrystallized again from benzene and ligroin mixture (1 to 1) and several times from hot n-heptane until finally a clean white crystals with a melting range of 135.5 to 137.0° (uncor.) were obtained. The yield of pure product was about 42% (32.5 g) based on the p-bromobiphenyl used. About 50% yield (based on benzophenone) has been reported.[29]

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30. H. Gilman and A. H. Haubein, ibid., 66, 1515 (1944).

A second preparation was done on the same scale as the previous one. Reaction of 37.1 (0.535 g-atom) of Li metal with 57.1 g (0.245 mole) of p-bromobiphenyl in 500 ml of dried ether gave 73% yield of p-biphenylyllithium according to Gilman titration and gave 72 g of crude yellow product after addition of 32.3 g (0.177 mole) of benzophenone in 100 ml of dried ether over a two hour period and subsequent steam distillation for 12 hours. The crude product was saved for combination with the product of the next preparation.

The third preparation, initiated by adding 5 drops of CH_3I, gave 70% yield of p-biphenylyllithium from the reaction of 68.2 g (0.292 mole) of p-bromobiphenyl in 700 ml of dried ether with 4.37 g (0.629 g-atom) of Li metal and yielded about 75 g of crude carbinol after addition of 35.1 g (0.193 mole) of benzophenone in 100 ml of dried ether over a period of one hour and steam distillation for 14 hours. The product was combined with that of the second preparation and recrystallized by the method given in the first preparation. The purified product was 75.4 (41.8% yield based on p-bromobiphenyl used) of almost white crystals (mp 136.0° - 137.2°).

The fourth preparation was carried out in a 2-l Morton flask equipped with the same apparatus as in the first preparation. p-Biphenylyllithium was prepared in 70% yield by reaction of 7.03 g (1.01 g-atom) of Li metal in 150 ml of dried ether with 93.1 g (0.399 mole) of p-bromobiphenyl in

500 ml of dried ether over a time period of two hours each for addition and reflux. A solution of 51.0 g (0.280 mole) of benzophenone in 150 ml of dried ether was added to this reaction mixture over a period of one hour and heated reflux for two hours. Then the adduct was treated with a solution of NH_4Cl and distilled with steam for 12 hours. The crude product amounted to about 116 g. This yellow material, after several recrystallizations from the same solvents as in previous runs, i.e., ligroin and n-heptane, gave 81.6 g of almost white crystaline solid, mp 135.5° - 137.0° (60.8% yield based on p-bromobiphenyl used).

In the fifth preparation, the reaction of 15.0 g (2.08 g-atom) of Li metal, 5 drops of CH_3I and 200 g (0.858 mole) of p-bromobiphenyl in 1-l of dried either in a 2-l Morton flask, gave about 75% yield of p-biphenylyllithium after at 75 minutes addition time and 2 hours at reflux. Addition of 126 g (0.689 mole) of benzophenone in 150 ml of dried ether to the reaction mixture was carried out over a period of 90 minutes. Then the adduct was heated at reflux for an hour until it was treated with a solution of NH_4Cl. After 12 hours of steam distillation, crude product was collected and recrystallized from ligroin to give 198 g of crude yellow crystals. Further recrystallization from n-heptane yielded 125 g of almost pure carbinol, mp 135.5 - 137.2° (48.2% yield based on p-bromobiphenyl used).

p-Biphenylyldiphenylchloromethane

This chloride was successfully prepared according to the procedure of Marvel and coworkers.[31] In a typical reaction, 75.4 g (0.224 mole) of pure p-biphenylyldiphenylcarbinol was dissolved in 300 ml of hydrogen chloride-free acetyl chloride (freshly distilled from dimethylaniline) and the mixture was heated at reflux for 3 hours in an all-glass apparatus equipped with a water condenser. After standing several hours tightly stoppered in a refrigerator, the reaction mixture was filtered through a sintered-glass funnel and the precipitate recrystallized from dry ligroin and washed with hot n-pentane. Additional chloride was obtained from the filtrate when it was further concentrated and kept in a refrigerator. The yield was 74.5 g (94.7 percent) of white crystals melting at 146.0 - 148.0°. In other similar preparations, the average yield of the chloride was 72.5 percent, mp 147.3 - 148.3°. (Lichtin reports[29] 147.0 - 147.8°, uncor.).

4-Chloro-1-p-biphenylyl-1,1-diphenylbutane

The titled compound was synthesized from the reaction of p-biphenylyldiphenylmethylsodium with excess 1-bromo-3-chloropropane. In the first run, p-biphenylyldiphenylmethylsodium was prepared according to the modified procedure of

31. C. S. Marvel, M. B. Mueller and E. Ginsberg, ibid., 61, 2008 (1939).

Renfraw and Hauser[32] from the reaction of powdered sodium amalgam (2.34 g of sodium and 101.0 g of mercury) with p-biphenylyldiphenyl chloromethane (20.8 g, 0.0586 mole) in 400 ml of dry ether in a 1-l reagent bottle with shaking on a mechanical shaker for 4 hours. The reaction mixture (deep red color) was siphoned under a nitrogen atmosphere into 100 ml of 1-bromo-3-chloropropane at room temperature over a period of five minutes. The color of p-biphenylyldiphenylmethylsodium disappeared instantly upon contact of this reaction mixture with 1-bromo-3-chloroprapane. Then the solution was kept overnight at room temperature. Next day the solution was separated from the muddy materials (inorganic product) which was sunk down to the bottom of the container by careful decantation. Some ether was added to the separated muddy materials, the mixture was filtered, and the filtrate was combined with the separated main solution. The solvent was removed in vacuo to give a yellow viscous material. Since attempted recrystallization of this crude product in several solvents, i.e., acetone, ligroin, n-pentane, n-hexane, cyclohexane, and ethanol, was not successful in this run, the product was combined later with that of another preparation.

In the second run, p-biphenylyldiphenylmethylsodium was prepared similarly from 74.5 g (0.210 mole) of p-biphenyl-

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32. W. B. Renfraw, Jr., and C. R. Hauser, Org. Syntheses, Collective Volume II, John Wiley & Sons, New York, 1861, p. 607.

yldiphenylchloride and sodium amalgam (8.80 g of sodium and 363 g of mercury) in 1000 ml of dry ether with shaking for 5 hours and was then reacted with 350 ml of 1-bromo-3-chloropropane under a nitrogen atmosphere. After standing overnight, the solution was separated from the muddy materials as the same way as above. Then the reaction solution was concentrated to dryness in vacuo to give yellow tarry materials. Recrystallization of this crude product from the hydrocarbon solvents listed in the previous run also was not successful.

In the third run, 44.1 g (0.125 mole) of p-biphenylyldiphenylmethylchloride was reacted for four hours with powdered sodium amalgam prepared from 6.38 g of sodium and 262 g of mercury in 150 ml of ether. Since the resulting deep red-colored p-biphenylyldiphenylmethylsodium solution was too viscous to be siphoned by means of nitrogen stream, it was poured into 200 ml of 1-bromo-3-chloropropane in a dry box under a nitrogen atmosphere. After standing overnight as usual, the solution was filtered through a sintered glass funnel and the filtrate was concentrated to dryness to give a yellow viscous oil. It was dissolved in petroleum ether (bp 30° - 60°) and kept in a refrigerator for an hour until the solution became cloudy. When it was shaken, a deep brown-colored oily material settled to the bottom of the flask. Then the upper layer was separated out from the oil layer by careful decantation and kept in a refrigerator. After a couple of hours, same oily material was formed and the super-

natant layer was separated again and kept in a refrigerator. This was repeated until no further oily material was formed. In the same way, deep brown oily material was eliminated from the combined product of the first and second preparations. Then the combined product solution of the three runs was concentrated to dryness *in vacuo* and then dissolved in excess of *n*-heptane and kept in a refrigerator for a week. The precipitate formed was separated by filtration to give 65 g of light yellow crystals of mp 91° - 100°. Recrystallization from acetone gave 56.5 g of colorless crystals mp 97° - 99°. Attempted vacuum sublimation of this compound was not successful. The analytical sample was further recrystallized from acetone and then twice from absolute ethanol and finally from *n*-heptane to give colorless crystals, mp 99.3° - 100.2° (new compound); nmr (CCl_4): δ 7.25 (19.0 H, m), 3.32 (1.9 H, t, J = 6.04 Hz) 2.72 (1.9 H, *ca.* t, J = 8.0 Hz), 1.58 (1.93 H, m

Anal.[*] Calcd. for $C_{28}H_{25}Cl$: C, 84.70; H, 6.35; Cl, 8.95. Found: C, 84.85, 84.95; H, 6.43, 6.30; Cl, 8.94, 8.96.

During the recrystallizations, 1.3 g of a substance (mp 165.5° - 167°) was obtained. This compound was not soluble in acetone and the nmr spectrum of this compound showed only an aromatic peak.

In the fourth run, *p*-biphenylyldiphenylmethylsodium was prepared from 112 g (0.313 mole) of *p*-biphenylyldiphenyl-

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[*] Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

methylchloride with powdered sodium amalgam (13.3 g of sodium and 546 g of mercury) in 1000 ml of dry ether for 4 hours. After cooling it down to room temperature, one fifth of the reaction mixture was reacted with 100 ml of 1-bromopropane to synthesize 1-p-biphenylyl-1,1-diphenylbutane while the rest of the reaction mixture was siphoned into the 500 ml of 1-bromo-3-chloropropane under a nitrogen atmosphere. Work-up of the product as in the previous run gave 47.5 g (47 percent) of nearly pure 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (mp 97.5° - 100°).

Synthesis of 1-p-Biphenylyl-1,1-diphenylbutane

This compound was synthesized from the reaction of 1-p-biphenylyldiphenylmethylsodium with 1-bromopropane. After reacting the former with the latter (see previous paragraph), the reaction mixture was filtered through a sintered glass funnel and the filtrate was concentrated to dryness *in vacuo* to give yellow oily material. Recrystallization and purification procedures were adopted from those of the 4-chloro-1-p-biphenylyl-1,1-diphenylbutane.

Yield of this compound was about 9.3 g (mp 92.5° - 94°) after recrystallization from n-heptane and acetone. The analytical sample was recrystallized once from absolute ethanol and twice from n-hexane to give white crystals, mp 94.7° - 95.3° (new compound); nmr (CCl_4): δ 7.23 (19.1 H, m), 2.52 (2.0 H, *ca.* t), 0.96 (5.0 H, broad, m).

Anal.* Calcd. for $C_{28}H_{26}$: C, 92.77; H, 7.23.
Found: C, 92.83, 92.92; H, 6.99, 7.09.

Synthesis of p-Biphenylyldiphenylmethane

Synthesis of the desired p-biphenylyldiphenylmethane was carried out using benzene as a co-solvent for the coupling reaction, according to the general procedure of Bachmann.[33]

In the first run, 2.66 g (0.110 g-atom) of magnesium turnings in 50 ml of dry ether was introduced into a flame dried 500 ml Morton Flask fitted with a high-speed stirrer, water condenser and dropping funnel and the system was kept under a nitrogen atmosphere. After adding about 0.5 ml of methyl iodide, the solution was stirred for 20 minutes at room temperature. And then 23.5 g (0.102 mole) of purified p-bromobiphenyl[24] in 200 ml of dry ether was added dropwise for 2 hours with continuous stirring at refluxing temperature. The reaction mixture was refluxed for an additional five hours until a 5 ml aliquot was analyzed. (The quantitative analysis[34] of the Grignard reagent was carried out by hydrolyzing an aliquot with water and titrating the resulting solution with the disodium salt of ethylenediaminetetraacetic acid to

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*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee

33. W. E. Bachmann, J. Amer. Chem. Soc., 55, 2135 (1933).

34. Dr. E. C. Ashby, private communication

an end point marked by Eriochrome Black T). The yield of Grignard reagent was about 71 percent. An hour later, to the solution of p-biphenylylmagnesium bromide in refluxing ether was added 15.8 g (0.0640 mole) of purified bromodiphenylmethane[25] in 100 ml of dry benzene over a period of 30 minutes and the reaction mixture was then heated at reflux for an hour with stirring. Unreacted Grignard reagent was destroyed by addition 150 ml of 5 percent hydrochloric acid. Insoluble solid in both aqueous and ether layer was removed by filtration. The separated ether phase of the filtrate was concentrated to dryness *in vacuo* to give a brown viscous material. This was dissolved in benzene and kept in a refrigerator. First formed precipitate was removed by filtration and recrystallized from benzene and acetone to give 2.8 g of white crystals (mp 210.5° - 212°) which was later found to be 1,1-2,2-tetraphenylethane by measuring mixed melting point (no depression) and comparing retention times in gas column chromatographic analysis with the authentic sample.[35] The filtrate was further concentrated, some n-heptane was added and the solution was stored in a refrigerator. The precipitate formed was removed by filtration and recrystallized from hot absolute ethanol and n-heptane to give 7.45 g (23.3 percent yield based on p-bromobiphenyl) of white crystals melt-

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35. Unpublished work of Yao-Ming Cheng, Georgia Institute of Technology.

ing at 110° - 112° (Gilman and Jones report[36] 111°).

In the second preparation, p-biphenylylmagnesium bromide prepared from the reaction of 47.2 g (0.202 mole) of p-bromobiphenyl with 4.61 g (0.190 g-atom) of magnesium turning in 500 ml of dry ether for 12 hours, was reacted with 24.1 g (0.0976 mole) of bromodiphenylmethane in 150 ml of dry benzene. After working up the reaction mixture, the yield of p-biphenylyldiphenylmethane was 12.4 g (19.3 percent based on p-bromobiphenyl), mp 109.5° - 112°. During the recrystallizations of product, 4.8 g of 1,1,2,2-tetraphenylethane (mp 211° - 212°) was obtained.

Synthesis of 5-p-Biphenylyl-5,5-diphenylpentanoic Acid 5-p-Biphenylyl-5,5-diphenylpentanenitrile

This nitrile was prepared following the general procedure of Cope and Metha.[37] In a typical preparation, 4.35 g (0.0110 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane, 0.951 g (0.0194 mole) of sodium cyanide and 1.86 g (0.0124 mole) of sodium iodide were dissolved in 300 ml of dimethyl sulfoxide in a 500 ml Erlenmeyer flask fitted with a tight stopper, and the resulting solution was stirred with a magnetic stirrer at room temperature for 10 days.

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36. H. Gilman and H. L. Jones, J. Amer. Chem. Soc., 51, 2840 (1929).

37. A. C. Cope and A. S. Metha, ibid., 86, 5626 (1964).

The light green-colored reaction mixture was poured into 300 ml of water in a 500 ml beaker. The solid formed was removed by filtration and washed with water to give 4.05 g of resin-like white compound (96.0 percent yield based on the chloride used). Attempted recrystallization of this cyanide from acetone, n-hexane, and many other hydrocarbon solvents was not successful. This hard resin-like cyanide was used to synthesize 5-p-biphenylyl-5,5-diphenylpentanoic acid without further purification.

5-p-Biphenylyl-5,5-diphenylpentanoic Acid

This synthesis was done by treatment of the corresponding nitrile with base according to the general procedure given in "Organic Syntheses".[38] A solution of 3.15 g (0.00815 mole) of 5-p-biphenylyl-5,5-diphenylpentanenitrile and 1.31 g (0.0234 mole) of KOH in 80 ml of ethylene glycol was heated at 220° for 6 hours. After cooling down to room temperature, the solution was diluted with 100 ml of water and then extracted with ether. The ethereal extract was washed with water. The combined aqueous phases were acidified with hydrochloric acid and extracted with ether. The ethereal extract was dried over anhydrous $MgSO_4$ and allowed to evaporate to dryness. These resulted 3.13 g (mp 97° -

38. Norman Rabjohn, Org. Syntheses, Collective Volume IV, John Wiley & Sons, Inc., New York, 1963, p. 95.

115°) of crude acid (94.5 percent yield based on the cyanide used). A portion of this acid, 0.982 g, was recrystallized twice from glacial acetic acid and once from n-hexane, and then dried in vacuum for one day at the temperature of boiling acetone to give 0.408 g of white crystals, mp 121.5° - 122.5° (new compound); nmr (CCl_4); δ 11.8 (1.03 H, s) 7.26 (19.0 H, m), 2.63 (2.04 H, ca. t, J = 7.5 Hz), 2.28 (2.05 H, t, J = 6.5 Hz), 1.46 (2.02 H, m).

Anal.* Calcd. for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.63, 85.83; H, 6.78, 6.85.

Synthesis of 5-p-Biphenylyl-2,2-diphenylpentanoic Acid 4-p-Biphenylyl-1,1-diphenylbutanol-1

This compound was synthesized from the reaction of phenylmagnesium bromide with methyl 4-p-biphenylylbutanoate according to the general procedure given in "Organic Syntheses".[39] In a flame-dried 500 ml Morton flask equipped with high-speed stirrer, dropping funnel and water condenser, 6.26 g (0.258 g-atom) of magnesium turnings in 20 ml of dry ether was introduced under an atmosphere of nitrogen. Approximately 5 ml of a solution of 39.6 (0.252 mole) of bromobenzene in 120 ml of dry ether was added at the beginning of

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

39. C. F. Allen and S. Converse, ibid., Collective Volume I, John Wiley & Sons, Inc., New York, 1948, p. 226.

the reaction and the reaction mixture was heated with vigorous stirring until the solution was at reflux. The reaction was initiated within one minute. The rest of the bromide solution in the dropping funnel was added over a period of 64 minutes. During the addition of bromide, the solution was not heated since the reaction was exothermal enough to maintain reflux. After the addition of bromide was completed, the mixture was stirred for 10 minutes and allowed to cool down to room temperature. A solution of 16.0 g (0.0630 mole) of methyl 4-p-biphenylylbutanoate* in 50 ml of dry ether was added dropwise with stirring for 10 minutes and the reaction mixture was stirred for an additional 10 minutes. A saturated solution of NH_4Cl in water was added; eventually the reaction mixture turned to a gelatinous material.

The mixture was extracted with ether four times and the combined ethereal extract was dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated to dryness *in vacuo* and dissolved in hot n-heptane. The precipitate which formed on cooling was separated by filtration and amounted to 18.8 g of white crystals, mp 101.2° - 103.0° (78.8 percent yield based on methyl-4-p-biphenylylbutanoate used). One recrystallization of 0.51 g of this carbinol from hot petroleum ether (bp 30° - 60°) afforded 0.36 g of

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*Prepared by Dr. S. Akabori, Georgia Institute of Technology.

white, needle-like crystals, mp 103.5° - 104.2° (new compound).

Anal.* Calcd. for $C_{28}H_{26}O$: C, 88.84; H, 6.87. Found: C, 88.84, 88.73; H, 7.02, 6.95.

1-Methoxy-4-p-biphenylyl-1,1-diphenylbutane

The 4-p-biphenylyl-1,1-diphenylbutanol-1 was converted to its methyl ether by the general procedure of Ziegler and coworkers.[40] 4-p-Biphenylyl-1,1-diphenylbutanol-1 (6.99 g, 0.0185 mole) was dissolved in 200 ml of absolute methanol and approximately 0.6 ml of concentrated sulfuric acid was added. The reaction mixture was stirred for 20 minutes at room temperature. After 3 minutes stirring, white crystals started to precipitate and the reaction mixture was continuously stirred for 20 minutes. The precipitate was removed by filtration and washed with absolute methanol to give 7.16 g of white crystals, mp 129.2° - 133° (without washing with methanol, the surface of the crystals turned red). One recrystallization from absolute methanol gave 6.67 g (92.0 percent based on the carbinol used) of white crystals melting at 113.7° - 136.0°. Analytical samples of this compound was recrystallized twice from absolute metha-

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

40. K. Ziegler, K. Richter, and B. Schnell, Ann., 443, 177 (1925).

nol and dried in vacuum (200 microns at acetone reflux temperature) for 6 hours. The melting point of this pure compound was 137.2° - 138.0° (new compound); nmr (CCl_4); δ 7.23 (19.0 H, m), 2.94 (3.0 H, s), 2.57 (2.0 H, t, J = 7.5 Hz), 2.28 (2.0 H, ca. t, J = 7.5 Hz), 1.44 (2.0 H, ca., quintet, J = 7.5 Hz).

Anal.* Calcd. for $C_{29}H_{28}O$: C, 88.72; H, 7.20. Found: C, 88.64, 88.89; H, 7.47, 7.37.

5-p-Biphenylyl-2,2-diphenylpentanoic Acid

The titled acid was prepared from the reaction of 1-methoxy-4-p-biphenylyl-1,1-diphenylbutane with molten potassium metal according to the procedure of Grovenstein and coworkers.[7] Into a flame-dried, 500 ml Morton flask equipped with a high-speed stirrer, a water condenser, and a dropping funnel, 250 ml of tetrahydrofuran which had previously been dried over sodium wire, was distilled from sodium aluminum hydride. The whole system was kept under a nitrogen atmosphere. After introducing 1.52 g (0.0390 g-atom) of potassium metal, the solvent was heated to the boiling point and refluxed for an hour with vigorous stirring. A solution of 6.68 g (0.0170 mole) of 1-methoxy-4-p-biphenylyl-1,1-diphenylbutane in 35 ml of distilled tetrahydrofuran was added dropwise over a period of 30 minutes. When the first drop of the ether was

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

added, a pink color instantly appeared in the solution and it changed to deep red as the reaction proceeded. Finally, the solution became deep black red. Stirring was continued for one hour at the reflux temperature of tetrahydrofuran. After cooling down to room temperature, about two thirds of the reaction mixture was forced onto a large excess of crushed solid carbon dioxide under a nitrogen atmosphere and excess methyl alcohol was added to the remainder of the reaction mixture in the flask. The next day, solvent was removed from the carbonated part *in vacuo* at steam-bath temperature and an aqueous potassium hydroxide solution was added to the residue. The solution was then extracted with ether; 1.31 g of neutral material was obtained from this ethereal solution. The separated aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. This ethereal solution was worked up and gave 4.22 g of crude acid, which yielded 3.27 g of white crystals melting at 186.0° - 188.5° after one recrystallization from glacial acetic acid. This acid was further purified from glacial acetic acid and *n*-hexane. After washing with hot petroleum ether (bp 30° - 60°), it was dried for 5 hours *in vacuo* at the temperature of boiling acetone. The resulting acid amounted to 2.56 g of nearly pure crystals (mp 191.4° - 191.8°) which proved (mixture mp and nmr) to be the same acid as that isolated from the reaction of 4-chloro-1-*p*-

biphenylyldiphenylbutane with potassium metal in boiling tetrahydrofuran (see page 53): nmr (CCl_4), δ 11.76 (0.9 H, s), 7.25 (19.00 H, m), 2.50 (4.0 H, m), 1.45 (2.0 H, m).

Synthesis of 4-p-Biphenylyl-1,1-diphenylbutane

This hydrocarbon was synthesized from the reaction mixture prepared above, i.e., the portion of the 4-p-biphenylyl-1,1-diphenylbutyl potassium solution treated with excess methanol. The resulting mixture was concentrated to dryness in vacuo to give 1.89 g of yellow solid, which was combined with 1.31 g of the neutral material separated from the carbonated part above. The combined material was dissolved in hot absolute ethanol and kept cool overnight. The precipitate which formed was separated by filtration to afford 2.27 g of light yellow colored crystals melting at 78.2° - 81.8°. After two recrystallizations from absolute ethanol, it gave 1.02 g of white crystals, mp 80.4° - 81.5°. For the analytical sample, a portion was further recrystallized from absolute methanol and dried in vacuo for four hours at the temperature of boiling acetone. The white powdered crystals, mp 81.5° - 82.3° (new compound) which were obtained to be the same hydrocarbon (by mixture mp, mixture IR, and nmr) as isolated from the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with potassium metal in boiling tetrahydrofuran; nmr (CCl_4): δ 7.08 (19.00 H, m), 3.83 (0.98 H, t, J = 7.5 Hz), 2.57 (1.97 H, t,

J = 7.5 Hz), 1.81 (4.04 H, broad m, apparently two overlapping peaks around δ 2.0, ca. quintet and δ 1.6, ca. quartet).

Anal.* Calcd. for $C_{28}H_{26}$: C, 92.76; H, 7.24. Found: C, 92.84, 92.65; H, 7.04, 7.25.

Reactions of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium

The reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with lithium metal carried out according to the procedure of Grovenstein and Williams.[4]

In run one, 250 ml of tetrahydrofuran (THF) was distilled from $NaAlH_4$ directly into a 500 ml Morton flask equipped with a high-speed stirrer, a water condenser, and a dropping funnel. Under an atmosphere of nitrogen, 1.87 g (0.269 g-atom) of lithium metal cut into small pieces and 0.1 ml of CH_3I were added at room temperature (addition of methyl iodide may have been incomplete). After the reaction mixture had been cooled down to -70°, 6.76 g (0.0170 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 20 ml of distilled THF was added with vigorous stirring. The reaction initiated in 20 minutes with development of an orange color, which gradually turned to deep red. After completion of addition the chloride (30 minutes), the reaction mixture was

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

stirred for an additional 90 minutes until a black color appeared around the neck of the flask. The appearance of this deep color is assumed to mean that a small amount of dark blue radical anion has been formed by the biphenylyl nuclei present and that the chloride has completely reacted with lithium metal. The solution was forced onto pulverized solid carbon dioxide. Water was added to the residual contents of the flask and the mixture was extracted with ether; the ether layer, after drying over anhydrous $MgSO_4$, was evaporated to dryness and the residue was taken up in benzene for gas chromatographic analysis (Hydrocarbon I). To the carbonated product was added aqueous NaOH solution and the solution was extracted well with ether (small amount of NaCl was added to break up emulsions). The ethereal solution yielded 2.05 g of neutral material after the usual work-up (Hydrocarbon II). The separated alkaline layer was acidified strongly with hydrochloric acid and extracted with ether. The ethereal extracts were dried over anhydrous $MgSO_4$ and evaporated to give 4.82 crude acid. A portion of the acid was converted to methyl esters by reaction with diazomethane prior to analysis by gas chromatography; this analysis at 268° showed only one component of 11 minutes retention time. Recrystallization of this acid several times from n-heptane and isooctane gave a white powdered material of undefined melting point, ca. 60° - 130°. Further, recrystallization of this acid from many other solvents (95%

ethanol, n-hexane, petroleum ether, carbon tetrachloride and acetone) did not improve its melting point. Since the nmr spectrum of this acid [nmr (CCl_4); δ 11.8 (1.05 H, s), 7.25 (19.0 H, m), 2.46 (4.01 H, m), 1.46 (2.1 H, m)] looked almost like that expected for 5-p-biphenylyl-5,5-diphenylpentanoic acid, the acid was sent for elemental analysis.

Anal.* Calcd. for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.54, 85.62; H, 6.64, 6.75.

Another gas chromatographic analysis at 262° later showed that this acid ester in fact consisted of two components in yield of 20.9% (18.6 minutes retention time) and 79.1% (19.6 minutes retention time), which were identified as methyl esters of 5-p-biphenylyl-2,2-diphenylpentanoic acid and 5-p-biphenylyl-5,5-diphenylpentanoic acid, respectively. The former acid was identical in retention time to that produced from the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with potassium (see page 53); the latter was identical in retention time with an authentic sample prepared by hydrolysis of the nitrile produced from reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with cyanide ion (see page 34). The gas chromatographic analysis of the protonated hydrocarbons (Hydrocarbon I, see Table 1) showed that it contained 69.0 percent of 1-p-biphenylyl-1,1-di-

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Table 1. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Metal (Run I)

Relative Retention Time	Peak Area Percent (Relative Percent Ratio: RH to R'H)		Identification
1. Neutral Materials	Hydrocarbon Fraction I	II	
0.55	0.3	2.0	unknown
1.00	3.20	2.0	p-$PhC_6H_4CH(Ph)_2$
1.21	1.1		unknown
1.48	69.0 (85.5)	77.4 (88.3)	p-$PhC_6H_4C(Ph)_2(CH_2)_2CH_3$
2.14	10.5 (14.5)	10.3 (11.7)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.38	2.9		unknown
2.54	1.3		unknown
2.81	11.8	8.2	p-$PhC_6H_4C(Ph)_2(CH_2)_3Cl$
2. Acidic Materials as Methyl Esters			
3.18	20.9		p-$PhC_6H_4(CH_2)_3C(Ph)_2COOH$
3.42	79.1		p-$PhC_6H_4C(Ph)_2(CH_2)_3COOH$

VPC conditions: Column (B); temperature 262°; flow rate, 52 mm; pressure, 40 psig.

phenylbutane (RH), 10.5 percent of 4-p-biphenylyl-1,1-diphenylbutane (R'H), 3.2 percent of biphenylyldiphenylmethane, 11.8 percent of unreacted chloride and a few percent of several unknowns (see Table 1). The analysis of the separated hydrocarbons (Hydrocarbon II) by gas chromatography are given in Table 1. The hydrocarbon to which the structure of 4-p-biphenylyl-1,1-diphenylbutane was assigned was identical in retention time to the major hydrocarbon obtained from reaction of the present chloride with potassium. The authentic sample of 1-p-biphenylyl-1,1-diphenylbutane was prepared by reaction of p-biphenylyldiphenylmethyl sodium with propyl bromide (see page 30). The minor cleavage product, p-biphenylyldiphenyl methane was identical in retention time with that of authentic sample prepared by reaction of p-biphenylyl magnesium bromide with bromodiphenylmethane (see page 31).

In run 2, into 250 ml of freshly distilled THF was placed 1.86 g (0.269 g-atom) of lithium metal which had been cut into small pieces and the solution was stirred vigorously at room temperature after addition of 0.05 ml of methyl iodide. The temperature was lowered to -70° and 7.27 g (0.0184 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 40 ml of freshly distilled THF was added over a period of 25 minutes. The solution developed a reddish brown color which deepened with continued stirring. After two more hours of stirring, the solution suddenly turned almost black over

a period of five minutes. The solution was forced through a glass siphon tube, mounted with a stainless steel fine mesh screen on one end (to remove excess lithium), into a flask for storage at 0° (ice bath). Water was added to the residual reaction mixture in the Morton flask and the mixture was extracted with ether. After drying over with anhydrous $MgSO_4$, the ether was removed *in vacuo* and the residue was dissolved in benzene for gas chromatographic analysis (Hydrocarbon III). The filtered tetrahydrofuran solution of organolithium compounds after standing 4 hours at 0° was forced onto excess crushed solid carbon dioxide, while water was added to the residue remaining in the flask. The hydrolysate was worked up as previously for gas chromatographic analysis (Hydrocarbon IV). Water (made alkaline with NaOH) was added to the carbonated product and the solution was extracted with ether. The alkaline layer was acidified with concentrated hydrochloric acid and extracted with ether. Both of the ethereal solutions were dried over anhydrous $MgSO_4$ and evaporated to yield 1.19 g of crude acid and 4.31 g of neutral materials (Hydrocarbon V). A portion of the acid was converted to methyl esters to analyze by gas chromatography; this analysis showed two peaks in ratio of 83.4 to 16.6 which are identified as methyl esters of 5-*p*-biphenylyl-2,2-diphenylpentanoic acid and 5-*p*-biphenylyl-5,5-diphenylpentanoic acid respectively. The ratio of unrearranged hydrocarbon (1-*p*-biphenylyl-1,1-diphenylbutane) versus re-

Table 2. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Metal (Run 2)

Relative Retention Time	Peak Area Percent (Relative % Ratio; RH to R'H)			Identification
1. Neutral Materials	Hydrocarbon Fractions III	IV	V	
1.00	0.8	1.1	0.5	p-$PhC_6H_4CH(Ph)_2$
1.21	2.8			unknown
1.49	66.4 (76.4)	54.3 (68.7)	60.7 (81.4)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.08	20.5 (23.6)	24.7 (31.3)	13.9 (18.6)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.44	4.4	8.0	9.5	unknown
2.71	4.8	6.6	9.5	p-$PhC_6H_4C(Ph)_2(CH_2)_3Cl$
3.05		5.2	6.0	unknown
2. Acidic Materials as Methyl Esters				
3.08	83.4			p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
3.46	16.6			p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$

VPC conditions: Column (B) temperature, 262°; flow rate, 52 mm; pressure 40 psig

arranged hydrocarbon (4-p-biphenylyl-1,1-diphenylbutane) obtained on gas chromatographic analysis of the Hydrocarbon III was a 76.4 to 23.6 and the ratio of the former and the latter hydrocarbon in the analysis of the Hydrocarbon IV was 68.7 to 31.3 (see Table 2). See also Table 2 for the analysis of the Hydrocarbon V. The identification of the hydrocarbons was done by the same methods as in run 1.

In run 3, reaction between 4-chloro-1-p-biphenylyl-1,1-diphenylbutane and lithium metal at -75° was carried out on the same scale and by the same technique as in run 2. A 0.5 ml portion of 6.96 g (0.0176 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 40 ml of distilled tetrahydrofuran and 0.03 ml of methyl iodide were added to 1.79 g (0.258 g-atom) of lithium metal in 270 ml of distilled tetrahydrofuran. After 32 minutes of stirring at -16° the solution turned to pink brown. The reaction temperature was lowered to -75° and the remainder of the chloride was added over a period of 10 minutes. The color of the solution changed to that of bromine. Stirring was continued for an additional two hours and 10 minutes until a black color appeared in the solution. About 170 ml of the solution was carbonated with filtration to remove excess lithium metal and about 100 ml of the solution was transferred under a nitrogen atmosphere to a 250-ml Erlenmeyer flask for storage at -11° (ice bath with NaCl). To the residual contents of the reaction flask was added water and the mixture was ex-

tracted with ether; the ethereal extract, after the usual work-up, was dissolved in benzene for gas chromatographic analysis (Hydrocarbon VI). The carbonated mixture was worked up as usual to give 1.18 g of neutral material (Hydrocarbon VII) and 4.22 g of acidic material (Acid I). After 8 hours storage at -11°, the transferred mixture was forced onto solid carbon dioxide through a siphon. To the residue in the flask was added water and the mixture was extracted with ether; the ethereal extract, after the usual work-up, was prepared for gas chromatographic analysis (Hydrocarbon VIII). The carbonated mixture yielded 0.17 g of acidic material (Acid II) and 2.33 g of neutral material (Hydrocarbon IX) when it was worked up in the usual way. Portions of Acids I and II were converted to methyl esters for analysis by gas chromatography. Analysis of Acid I showed two acid components of 77.9 and 22.1 percent which are identified as methyl esters of unrearranged acid (RCOOH) and rearranged acid (R'COOH) respectively. Analysis of Acid II gave 26.1% of RCOOH and 73.9% of R'COOH. Gas chromtographic analysis of Hydrocarbon VI revealed that, among the volatile components, the ratio of the RH versus R'H was a 76.1 to 28.4. Analysis of Hydrocarbon VIII gave a 67.5 to 32.5 ratio of RH to R'H. Analytic results for this run are summarized in Table 3.

Table 3. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Metal (Run 3)

Relative Retention Time	Peak Area Percent (Relative % Ratio; RH to R'H)				Identification
1. Neutral Materials	Hydrocarbon Fraction VI	VII	VIII	IX	
0.50	9.7	0.3	9.9	0.2	unknown
1.00	1.0	3.8	1.1	0.8	p-$PhC_6H_4C(Ph)_2H$
1.20	6.4				unknown
1.52	54.5	76.6	50.0	64.8	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
	(76.1)	(85.5)	(67.5)	(77.2)	
2.11	21.6	12.9	24.1	19.1	p-$PhC_6H_4(CH_2)_3CH(Ph_2)$
	(28.4)	(14.5)	(32.5)	(22.8)	
2.36	6.9	6.5	6.7	5.9	unknown
3.20			8.3	9.2	unknown

VPC conditions: Column (A) temperature, 252°;
flow rate, 20 mm; pressure, 40 psig

Table 3. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Metal (Run 3) (Continued)

Relative Retention Time	Peak Area Percent (Relative % Ratio; RH to R'H)		Identification
2. Acidic Materials as Methyl Ester			
	Acid Fraction I	II	
21.2	77.9	26.1	p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
23.2*	22.1	73.9	p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$
VPC conditions: Column (B) temperature, 252°; flow rate, 50 mm; pressure, 40 psig			

*Actual retention time in minutes

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium Metal

The reaction of the chloride with potassium metal was carried out according to the procedure of Grovenstein and coworkers.[7]

In run 1, into a 250 ml Morton flask, 130 ml of tetrahydrocarbon was freshly distilled from lithium aluminum hydride under a nitrogen atmosphere. Potassium metal (0.99 g, 0.0254 g-atom) was added, the contents were heated to reflux temperature, and the mixture was stirred vigorously for 2 hours (potassium metal was divided into fine particles). Vigorous stirring was continued while 4.13 g (0.0104 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 30 ml of freshly distilled tetrahydrofuran was added over a period of ten minutes. An instant red color appeared upon addition of the chloride and the solution was soon black red. The solution was allowed to cool for eight minutes and then forced onto excess solid carbon dioxide. Methyl alcohol was added to the residual contents of the flask and the mixture was heated at reflux a few minutes to decompose traces of potassium.

After the usual work-up, the methanolysis was prepared for gas chromatographic analysis (Hydrocarbon I). The carbonated mixture yielded 3.40 g of acids and 1.24 g of neutral materials (Hydrocarbon II). Gas chromatography upon the methyl ester of a small portion of the acid fraction showed

only one peak (22.9 min.) of shorter retention time than that of an authentic sample of methyl 5-p-biphenylyl-5,5-diphenylpentanoate (25.0 min.). The new ester peak is assigned to methyl 5-p-biphenylyl-2,2-diphenylpentanoate. Analysis of Hydrocarbon I by gas chromatography gave a 98.9 to 1.14 ratio of rearranged hydrocarbon (4-p-biphenylyl-1,1-diphenylbutane) to unrearranged hydrocarbon (1-p-biphenylyl-1,1-diphenylbutane). Analytical results upon Hydrocarbon II are given in Table 4. Recrystallization of a 2.0 g portion of the crude acid two times from glacial acetic acid and then from n-hexane yielded 1.4 g of white crystals of mp 191.5 - 192.0° (new compound). The nmr spectrum in CCl_4, δ 7.25 (19.00 H, broad multiplet, aromatic hydrogens), 2.50 (4.03 H, complex multiplet attributed to two overlapping triplets, methylene groups next to biphenylyl and carboxylic groups), 1.45 (2.01 H, complex multiplet), agrees with that expected for 5-p-biphenyly-2,2-diphenylpentanoic acid.

Anal.* Calcd. for $C_{28}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.67, 85.45; H, 6.72, 6.71.

In run 2, tetrahydrofuran (150 ml) and 0.278 g (0.00711 g-atom) of freshly cut potassium metal were placed in a Morton flask. The mixture was heated at reflux with vigorous stirring for an hour and then a solution of 1.037 g (0.00261

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Table 4. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium (Run 1)

Relative Retention Time	Peak Area Percent (Relative % Ratio: RH to R'H)		Identification
1. Neutral Materials	Hydrocarbon Fraction I	II	
0.51	6.2	4.1	unknown
1.00	3.8	1.5	p-$PhC_6H_4CH(Ph)_2$
1.54	0.95 (1.14)	4.6 (4.84)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.12	82.4 (98.9)	89.9 (95.2)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.78	6.7		unknown
VPC conditions: Column (A) temperature, 254°; flow rate, 20 mm; pressure, 40 psig			
2. Acidic Materials as Methyl Ester			
22.9**	100		p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
25.0*	0		p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$*
VPC conditions: Column (B) temperature, 254°; flow rate, 50 mm; pressure, 40 psig			

*Used as a standard for comparison

**Actual retention time

mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 20 ml of distilled tetrahydrofuran was added over a period of 10 minutes through the dropping funnel. On addition of the first portion of the halide, the solution turned a deep red; the final color was like that of bromine. After cooling to room temperature in 10 minutes (without stirring), an excess of methyl alcohol (30 ml) was added dropwise to the reaction mixture with stirring over a period of 5 minutes. The next day, solvents were removed in vacuo, water was added to the residual viscous materials, and the mixture was extracted with three 100 ml portions of ether. The ether extract, after drying over anhydrous $MgSO_4$, yielded 1.10 g of crude oil materials. A small portion of this material was dissolved in n-heptane for gas chromatographic analysis. Analysis (VPC) of the hydrocarbons gave the following products, listed as area percent: 0.8 of unknown, 0.14 of p-biphenylyldiphenylmethane, 1.36 of 1-p-biphenylyl-1,1-diphenylbutane and 97.7 of 4-p-biphenylyl-1,1-diphenylbutane respectively (see Table 5). Recrystallization of the crude material once from n-heptane and twice from 95% ethanol and subsequent vacuum sublimation at 0.3 mm at a bath temperature 135° for 4 hours gave 0.15 g of white solid melting at 80.0 - 81.3°. This was again recrystallized from 95% ethanol, absolute methanol and finally from petroleum ether (bp 30 - 60°) to give 0.022 g of white powdered crystal, mp 81.2 - 82.0°. This compound

Table 5. Gas Chromatographic Analysis of Product from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium (Run 2)

Relative Retention Time	Peak Area Percent (Relative Ratio: RH to R'H)	Identification
0.52	0.82	unknown
1.00	0.14	p-$PhC_6H_4CH(Ph)_2$
1.59	1.36 (1.4)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.25	97.7 (98.6)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$

VPC conditions: Column (A) temperature, 256°; flow rate, 40 mm; pressure, 40 psig

was identified as 4-p-biphenylyl-1,1-diphenylbutane based on the nmr spectrum of authentic sample;nmr (CCl_4) δ 7.08 (19.00 H, complex multiplet, 3.83 (1.0 H, triplet, J = 7.5 Hz), 2.57 (2.0 H, triplet, J = 7.5 Hz), 1.81 (4.4 H, broad multiplet).

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cesium Metal

Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with cesium metal in tetrahydrofuran was carried out according to the procedure of Grovenstein and coworkers.[7]

The usual apparatus was set up in a glove box and was flame dried. The box, after sweeping out with a nitrogen stream, was kept under an atmosphere of nitrogen. Tetrahydrofuran (150 ml) was distilled directly into a 300 ml Morton flask from lithium aluminum hydride and 2.21 g (0.0166 g-atom) of Cs metal was introduced. The mixture was heated to reflux. Upon stirring the solution developed a pale blue color. After vigorous stirring for 30 minutes a solution of 3.00 g (0.00757 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 20 ml of distilled tetrahydrofuran was added to the reaction mixture at reflux temperature over a period of 2 minutes. A dark red (almost black) color rapidly developed in the solution. Stirring was continued for two more minutes before the reaction mixture was forced onto the crushed solid carbon dioxide. To the small resi-

Table 6. Gas Chromatographic Analyses of Products in Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cesium Metal at 65°

Relative Retention Time	Peak Area Percent (Relative % Ratio: RH to R'H)		Identification
1. Neutral Materials	Hydrocarbon Fraction I	II	
0.38		2.5	unknown
1.00	2.50	4.4 (4.5)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.38	97.5	93.0 (95.5)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2. Acidic Materials as Methyl Ester			
2.23	100		p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
2.40*	0		p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$

VPC conditions: Column (A) temperature, 257°; flow rate, 24 mm; pressure, 40 psig

*Relative retention time of standard authentic methyl ester of 5-p-biphenylyl-5,5-diphenylpentanoic acid.

dual contents in the flask was added excess methanol (Hydrocarbon I). The usual work-up gave 2.60 g of solid acids and and 0.405 g of crude neutral material (Hydrocarbon II). Gas chromatographic analysis of the protonated hydrocarbon (Hydrocarbon I) showed two components, i.e., 2.5% of unrearranged hydrocarbon and 97.5% of rearranged hydrocarbon. Analysis of Hydrocarbon II is given in Table 6. Analysis of the methyl ester of the acid by gas chromatography gave only one product which is identified as the methyl ester of 5-p-biphenyl-2,2-diphenylpentanoic acid. A portion of the acid was recrystallized from glacial acetic acid and n-hexane to give white crystals, mp 190.2 - 191.2. This compound is identified as the rearranged acid (R'COOH) based on melting point, mixture melting point and nmr spectrum: nmr (CCl_4), 7.25 (19.00 H, m), 2.50 (4.1 H, m), 1.45 (2.1 H, m).

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Sodium in Dioxane

In run 1, into the usual apparatus for organoalkali metal reactions, 150 ml of dioxane (which had previously been purified according to the general procedure of Fieser[27]) was distilled from sodium metal and 0.442 g (0.0192 g-atom) of freshly cut sodium metal was introduced. The mixture was heated at reflux with vigorous stirring for one hour and then a small portion (2 ml) of a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (3.50 g, 0.00883 mole) in 30

ml of distilled dioxane was added. Since no color change was observed in 20 minutes, 0.23 g of methyl iodide (0.8 mmole) and 0.21 g (0.71 mmole) of 2-chloro-1,1,1-triphenylethane in distilled dioxane was introduced through another dropping funnel over a period of 20 minutes. Upon addition of this halide mixture, the solution instantly developed a light gray-violet color which gradually turned to violet on continued vigorous stirring. The remaining chloride solution was added dropwise for 20 minutes until about 5 ml was left in the dropping funnel (after concentration to dryness, the chloride left in the funnel weighed 0.49 g). The reaction mixture was kept at reflux with vigorous stirring for an additional 30 minutes. After cooling down to room temperature, the mixture was forced onto solid carbon dioxide and excess water was added to the small remainder in the flask (Hydrocarbon I). The carbonated product was worked up as usual to give 3.27 g of neutral material (Hydrocarbon II) but no acid was obtained. According to the gas chromatographic analysis at 254°, both of the hydrocarbon fractions (Hydrocarbon I and II) showed only unrearranged hydrocarbon (96.4% of each) with 3.4% of unreacted chloride.

In run 2, 2.77 g (0.120 g-atom) of sodium metal was placed in 150 ml of freshly distilled dioxane (previously purified by the method given by Fieser) from molten sodium metal and the mixture was stirred at reflux for one hour. A solution of 3.34 g (0.0361 mole) of n-BuCl in 20 ml of

distilled dioxane was added dropwise to dry the solution over a 15 minute period. On addition of the first portion of the halide, the solution turned to a violet; the final color of the solution after the addition was deep violet. Then a solution of 0.144 g (0.5 mmole) of 2-chloro-1,1,1-triphenylethane in 10 ml of distilled dioxane was added for the purpose of an indicator (no color change was observed in 5 minutes). Addition of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.83 g, 0.00461 mole) in 150 ml of distilled dioxane for 20 minutes did not cause any appreciable color change. The mixture was stirred at reflux vigorously for an additional 30 minutes. After cooling down to room temperature, the mixture was siphoned onto crushed solid carbon dioxide with a stream of nitrogen. To the small residual contents in the reaction flask was added excess ethanol (Hydrocarbon III). The usual work-up of the carbonated mixture gave 1.80 g of crude neutral material (Hydro arbon IV) but no acid was obtained. Gas chromatographic analysis (256°) fo the both hydrocarbon fractions (Hydrocarbon III and IV) in n-heptane gave essentially the same result for their product compositions: 92% of unrearranged hydrocarbon and 8% of rearranged hydrocarbon. Fractional recrystallization of 1.75 g of the crude material from n-heptane gave 1.15 g of white crystalline solid, mp 88 -93° (rearranged hydrocarbon has greater solubility in n-heptane than unrearranged hydrocarbon). The solid was further purified

twice from n-heptane and once from absolute ethanol to give 0.24 g of white crystals, mp 94.2 - 95.0°, which was identified as 1-p-biphenylyl-1,1-diphenylbutane by the comparisons of melting point, mixture melting point, VPC retention time, and nmr spectrum with those of an authentic sample prepared by treating p-biphenylyldiphenylmethyl sodium with 1-chloropropane. The nmr spectrum provided a confirmatory evidence: nmr (CCl_4) δ 7.23 (19.00 H, multiplet, aromatic hydrogens), 2.52 (1.90 H, ca. triplet, CH_2 group next to p-biphenylyldiphenylmethyl group), 0.96 (4.93 H, overlapped multiplet, terminal CH_2CH_3 group).

In run 3, two sets of the usual apparatus were arranged side by side so that solvent could be distilled from one flask into the other. Into the first flask, 400 ml of dioxane, previously purified by the method listed by Fieser was distilled from molten sodium and about 3 g of freshly cut potassium metal was added. The mixture was stirred vigorously at reflux for an hour then 250 ml of the solvent distilled into the second flask over a period of 45 minutes with continued stirring. To the second flask was added 2.28 g (0.0993 g-atom) of freshly cut sodium metal and the mixture was heated at reflux with high-speed stirring for one hour. A solution of n-BuCl (3.29 g, 0.0356 mole) in 20 ml of distilled dioxane was added dropwise to the mixture over a period of 15 minutes. On addition of the first portion of the halide the solution instantly developed a

grape color (deep violet) and the solution was continously stirred. Then a solution of 2-chloro-1,1,1-triphenylethane (0.15 g, 0.000513 mole) in 20 ml of distilled dioxane was added drop by drop for 5 minutes. Addition of the halide did not produce any color change. This was followed by the addition of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (2.096 g, 0.0053 mole) in 20 ml of distilled dioxane over a period of 15 minutes and the mixture was stirred at reflux for an additional hour (no color change was observed). After cooling to room temperature, a 10 ml aliquot was withdrawn and hydrolyzed with methanol (Hydrocarbon V). The mixture in the flask was forced onto the crushed solid carbon dioxide and the small residual contents in the flask was decomposed by the addition of excess methanol. The carbonated mixture was concentrated under partial vacuum, was poured into 100 ml of water, and extracted with four 100 ml portions of ether. The ethereal extracts were combined and washed with three 100 ml portions of water. After drying with anhydrous $MgSO_4$, the ethereal solution was concentrated to dryness *in vacuo* to give 1.77 g of crude oily neutral material (Hydrocarbon VI). The separated aqueous layer after acidification with concentrated hydrochloric acid was extracted with three 100 ml portions of ether and the combined ethereal extracts were dried with anhydrous $MgSO_4$ and filtered. After evaporating the ether, there was obtained 0.03 g of yellow oily liquid. A portion of the oily

liquid was converted to methyl ester with diazomethane and subjected to gas chromatographic analysis but no acid ester peak was obtained. Both of the hydrocarbon fractions (Hydrocarbon V and VI) were prepared for gas chromatographic analysis. According to the analysis, Hydrocarbon V was found to contain 8.0% of p-biphenylyldiphenylmethane, 2.6% of unknown, 84.2% of unrearranged hydrocarbon and 5.2% of rearranged hydrocarbon. Gas chromatographic analysis of Hydrocarbon VI is given in Table 7.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Dioxane

Into a 250 ml flask, 150 ml of dioxane which had been purified as usual was distilled from molten potassium under an atmosphere of nitrogen and 4.79 g (0.123 g-atom) of freshly cut potassium metal was added. The mixture was heated at reflux with vigorous stirring for 30 minutes. A solution of n-BuCl (2.87 g, 0.031 mole) in 20 ml of distilled dioxane was added dropwise over a period of 15 minutes. On addition of the n-BuCl solution a gray-blue color appeared within 30 seconds. To the reaction mixture was added a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (2.02 g, 0.00509 mole) in 20 ml of distilled dioxane over a period of 20 minutes. During the addition of chloride the color of the solution turned light blue at first and then changed to green, gray-pink and violet. When the addition

Table 7. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Sodium Metal in Dioxane (Run 3)

Relative Retention Time	Peak Area Percent (Relative % Ratio: RH to R'H)		Identification
	Hydrocarbon Fraction V	VI	
1.00	8.0	4.5	p-$PhC_6H_4CH(Ph)_2$
1.20	2.6	1.8	unknown
1.53	84.2 (94.2)	88.4 (94.3)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.03	5.2 (5.8)	5.3 (5.7)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$

VPC conditions: Column (A) temperature, 263°; flow rate, 20 mm; pressure, 40 psig

of the chloride was slowed down, the green color appeared again in the solution. Rapid addition of the chloride brought about development of a reddish brown color in the solution and finally the color turned deep red at the end of the chloride addition. The reaction mixture was heated at reflux for an additional one minute with vigorous stirring continued. After cooling to room temperature for 10 minutes, the mixture was forced through a glass siphon tube onto crushed solid carbon dioxide by means of nitrogen and the small residual mixture of the flask was protonated by excess ethanol. The protonated material was diluted with 100 ml of water and extracted with ether. After drying with anhydrous $MgSO_4$, the extract was concentrated to dryness, and dissolved in acetone for gas chromatographic analysis (Hydrocarbon I). In this analysis the relative percent yield of several minor components could not be calculated due to the unstable base line of the chromatograph but rearranged hydrocarbon (4-p-biphenylyl-1,1-diphenylbutane) was found as a major component and no unrearranged hydrocarbon was detected. After the usual work-up, the carbonated product gave 0.57 g of acidic material and 1.45 g of neutral material (Hydrocarbon II). Gas chromatographic analysis of "Hydrocarbon II" is given in Table 8, in which the absolute yield of rearranged hydrocarbon (R'H) was calculated as 75% by weight (quantitative VPC analysis based on a known amount of authentic sample) and unrearranged hydrocarbon (RH) was

Table 8. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Dioxane

Relative Retention Time	Peak Area Percent		Identification
1. Neutral Materials	Hydrocarbon Fraction I	II	
0.45	unmeasurable	1.3	unknown
0.52	"	3.44	"
0.71	"	3.47	"
0.87	"	2.03	"
1.00	"	1.62	p-$PhC_6H_4CH(Ph)_2$
1.94	86	77.3 (75%)[a]	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.90	14	10.8	unknown

Retention time based on p-$PhC_6H_4CH(Ph)_2$

2. Acidic Materials as Methyl Esters			
0.15	6.2		unknown
0.24	7.0		"
0.28	6.2		"
0.41	10.3		"

Table 8. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Dioxane (Continued)

Relative Retention Time	Peak Area Percent	Identification
2. Acidic Materials as Methyl Esters		
0.59	1.7	unknown
0.73	5.4	"
0.92	5.8	"
1.00	8.3 (8.7 mg)[b]	p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.29	39.3	unknown
1.63	9.9	"

Retention time based on methyl ester of p-$PhC_6H_4(CH_2)_3(Ph)_2CO_2H$

VPC conditions: F&M 810; SE-30 (10%); Column (B) temperature, 300°; flow rate, 20 mm; pressure, 40 psig

[a]Absolute percent yield in the "Hydrocarbon II".

[b]Absolute yield calculated based on authentic sample.

not found. Quantitative gas chromatographic analysis of methyl esters of the acid gave only 8.7 mg (0.324% based on the chloride used) yield of rearranged acid (R'COOH) with many other unknowns (see Table 8).

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cesium in Dioxane

In run 1, the usual apparatus (including a 500 ml Morton flask, a high-speed stirrer, a Vigreux column and a dropping funnel) was set up in a glove box. After drying the apparatus with a flame under an atmosphere of nitrogen the box was swept with nitrogen until no air was detected by flame ignition test. Into the flask 250 ml of purified dioxane (see other organoalkali metal reactions in dioxane) was distilled slowly from molten potassium (rapid distillation decomposed the dioxane). The solvent was heated to 40° before 5.02 g (0.0378 g-atom) of cesium metal was introduced. On addition of the cesium metal, the solvent around the cesium metal turned a cloudy white with some gas evolution. The mixture was stirred for 30 seconds and finally the entire solution became cloudy white. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.00 g, 0.00252 mole) in 20 ml of distilled dioxane was dumped into the solution at one time with vigorous stirring. The solution developed a red color instantly upon addition of the chloride and the color turned green-gray immediately. The

mixture was stirred vigorously for an additional 30 seconds before a 5 ml aliquot of the mixture was hydrolyzed with methanol. The reaction mixture was forced onto a crushed solid carbon dioxide through a glass siphon tube and to the small residue in the flask excess ethanol was added to decompose the residue. After the usual work-up, the carbonated material was found to contain only neutral material (0.895 g). The methanolysate was extracted with ether; after drying with anhydrous $MgSO_4$, the ethereal extract was concentrated and dissolved in acetone for gas chromatographic analysis (Hydrocarbon I). According to the analysis the protonated hydrocarbon gave 3.7% of 1-p-biphenylyl-1,1-diphenylbutane, 1.4% of p-cyclohexylphenyl-1,1-diphenylbutane (same retention time as that of next run), 89.3% of 4-p-biphenylyl-1,1-diphenylbutane and 5.7% of unreacted chloride. A portion of the neutral material which was obtained from the carbonated product was prepared for gas chromatographic analysis (Hydrocarbon II). The quantitative VPC analysis gave essentially the same result as that for Hydrocarbon II (see Table 9). The nmr spectrum of a portion of the crude product was measured in CCl_4 and the spectrum was identical except for small minor impurities (possibly Birch reduction impurities) with that of pure 4-p-biphenyl-1,1-diphenylbutane (see page 40); nmr (CCl_4), δ 7.1 (19.0 H, m), 3.83 (0.8 H, t), 2.57 (2.1 H, t), 1.81 (5.2 H, broad m, apparently two over-

Table 9. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cesium in Dioxane (Run 1)

Relative Retention Time	Peak Area Percent (Abs. Yield in g, Mol% Yield)		Identification
	Hydrocarbon Fractions		
	I	II	
1.00	3.7	3.58 (0.0298, 3.26)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.12	1.4	1.29 (0.0107, 1.16)	4-p-Cyclohexylphenyl-1,1-diphenylbutane*(?)
1.38	89.3	89.4 (0.742, 81.3)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
1.84	5.7	5.71 (0.0664, 6.62)	Unreacted chloride

VPC conditions: Column (A) temperature, 269°; flow rate, 13.5 mm.

*Retention time is same as that of 4-p-cyclohexylphenyl,1-diphenylbutane in run 2.

lapping peaks around δ 2.0, ca. quintet and δ 1.6, ca. quartet and some contributions from impurities).

In run 2, 5.10 g (0.384 g-atom) of cesium metal was introduced into 250 ml of dioxane (purified and distilled as in run 1) at 30° and the mixture was stirred for one minute (solution turned cloudy white. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (0.974 g, 0.00246 mole) in 20 ml of distilled dioxane was added in one second and the mixture was stirred for 5 minutes until a 5 ml aliquot was hydrolyzed with methanol (Hydrocarbon III). Upon stirring for one minute the temperature of the solution rose to 37° and a deep brown-pink color appeared in the solution. To the remaining reaction mixture was added another 5.21 g (0.0392 g-atom) of cesium metal and the mixture was stirred for 10 minutes (deep red). A 10 ml of aliquot was hydrolyzed with methanol (Hydrocarbon IV) before the both of the reaction mixtures were forced onto a crushed carbon dioxide through a glass siphon tube. After the usual work-up, the carbonated mixture yielded 0.618 g of neutral material (Hydrocarbon V) and 0.266 g of acids. A portion of the acids was transformed to methyl esters prior to gas chromatographic analysis. According to the quantitative VPC analysis most of the acid esters were non-volatile components and only 0.13% (based on the chloride used) of rearranged acid ester was detected among the several unknowns (see Table 10). Gas chromatographic analysis of Hydrocarbon III gave 0.6% of

4-p-cyclohexylphenyl-1-phenylbutane (compound A), 3.6% of 1-p-cyclohexylphenyl-1,1-diphenylbutane (compound B), 82.3% of 4-p-cyclohexylphenyl-1,1-diphenylbutane (compound C) and 13.5% 4-p-biphenylyl-1,1-diphenylbutane (R'H). On the other hand, VPC analysis of Hydrocarbon VI yielded 3.0% of Compound D (p-cyclohexyldiphenylmethane), 28.0% of Compound A, 1.0% of Compound B, 53.0% of Compound C and 15% of rearranged hydrocarbon (R'H). Quantitative VPC analysis of Hydrocarbon V are given in Table 10. A small portion of each Compound A, B, C, and D were collected separately in capillary tubes during VPC analyses and were analyzed with a mass spectrometer.

The molecular ion peak of Compound A was at 292 and base peak appeared at 91 (apparently the benzyl or tropylium cation) and the second abundant peak was at 117 ($Ph-\overset{+}{C}H-CH=CH_2$). The other significant peaks were at 104 ($C_6H_4-\overset{+}{C}H=CH_2$), 131 ($C_6H_4-\overset{+}{C}H-CH=CH_3$), 159 (phenylcyclohexyl cation), 173 (p-cyclohexylbenzylium cation or cyclohexyltropylium cation), 201 (3-p-cyclohexylphenylpropyl cation) and etc. According to the above mass spectrum Compound A was assigned the structure of 4-p-cyclohexylphenyl-1-phenylbutane (new compound).

Molecular ion peak of Compound C was 368 and base peak was at 167 (diphenylmethyl cation or phenyltropylium cation). The other significant peaks were at 91 (benzylium or tropylium cation), 159 (cyclohexylphenyl cation), 28 (ethylene cation), 77 (phenyl cation), 78 (benzene cation),

83 (cyclohexyl cation), 104 (styrene cation), 117 (phenylallyl cation), 173 (cyclohexyltropylium cation), 152, 165, 249, 285, 319 and etc. Based on the above spectral data Compound C is 4-p-cyclohexylphenyl-1,1-diphenylbutane (new compound).

Mass spectrum of Compound D showed its molecular ion at 250 and base peak was at 249 (p-cyclohexyldiphenylmethyl cation). The second highest peak was at 91 (benzyl or tropylium cation) and the others were at 165 and 167 (diphenylmethyl cation) and etc. Therefore, Compound D was identified as p-cyclohexyldiphenylmethane (new compound based on the above mass spectral data.

Mass spectrum of Compound B was identical with that of 1-p-cyclohexylphenyl-1,1-diphenylbutane (new compound) which was identified in reaction of 4-p-biphenylyl-1,1-diphenylbutane with potassium metal in presence of excess t-butyl alcohol (see page 80).

The crude neutral material (Hydrocarbon V) was dissolved in 100 ml of CCl_4 and the solvent was evaporated to dryness in vacuo. A portion of this material was prepared for nmr spectrum in CCl_4 solvent with TMS as internal standard; nmr (CCl_4); δ 7.1 (31.5 H, complex multiplet, aromatic hydrogens), 3.86 (1.0 H, triplet, J = 7.5 Hz), unique hydrogen on carbon attached to two phenyl groups), 3.23 (1.5 H, multiplet, unknown hydrogens), 2.57 (8.8 H, ca. triplet, one of methylene hydrogens near aromatic group),

Table 10. Gas Chromtographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cesium in Dioxane (Run 2)

Relative Retention Time	Peak Area Percent (Abs. Yield in g, Mol% Yield)			Identification
1. Neutral Materials	Hydrocarbon Fractions III	IV	V	
1.00		3	2.9	p-cyclohexyldiphenylmethane
1.3	0.6	28	32.1 (0.084, 11.7)	4-p-cyclohexylphenyl-1-phenylbutane
3.0	3.6	1	1.2 (0.0031, 0.34)	1-p-cyclohexylphenyl-1,1-diphenylbutane
4.3	82.3	53	54.1 (0.14, 15.6)	4-p-cyclohexylphenyl-1,1-diphenylbutane
5.3	13.5	15	9.7 (0.025, 2.84)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$

VPC conditions: Column (A) temperature 264°; flow rate 13.5 mm.

Table 10. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cesium in Dioxane (Run 2) (Continued)

Relative Retention Time	Peak Area Percent (Abs. Yield in g, Mol% Yield)	Identification
2. Acidic Materials as Methyl Esters		
0.26	14.7	unknown
0.51	25.7	"
0.8	13.8	"
1.00	17.4 (0.0013, 0.13)	p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.38	28.4	unknown

VPC conditions: Column (A) temperature, 264°, flow rate 13.5 mm.

1.63 (48 H, multiplet, cyclohexyl and two other methylene hdyrogens), 0.93 (trace H, ending methyl hydrogens). According to the nmr spectrum, the methyl group hydrogens of unrearranged hydrocarbon had almost disappeared while a unique hydrogen on carbon attached to two phenyl groups as expected for the rearranged hydrocarbon was clearly shown as a triplet and some evidence was found for cyclohexyl hydrogens at 1.63.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Presence of n-Butylamine

In the usual apparatus for organoalkali metal reactions was placed 120 ml of tetrahydrofuran (distilled from $NaAlH_4$) and 0.225 g (0.00576 g-atom) of freshly cut potassium. The mixture was stirred at reflux with vigorous stirring for 30 minutes and then a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.08 g, 0.00273 mole) and n-butylamine (0.912 g, 0.0125 mole) in 30 ml of distilled THF was added at one time without stirring. On addition of this mixture, the reaction mixture developed a deep red color instantly and the solution was stirred for one-half minute until 20 ml of methyl alcohol was added. The color of the solution disappeared instantly when the alcohol was added. The resulting mixture was stirred vigorously at reflux for an additional 10 minutes. After cooling to room temperature, the mixture was hydrolyzed with water. The usual work-up gave

1.04 g of crude material. A portion of this material was subjected to gas chromatographic analysis and was found to consist of 95.3% of rearranged hydrocarbon (4-p-biphenylyl-1,1-diphenylbutane) and 4.5% of non-rearranged hydrocarbon (1-p-biphenylyl-1,1-diphenylbutane) and less than 0.2% of p-biphenylyldiphenylmethane based on their relative peak area percent (see Table 11).

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Presence of Triethylcarbinol

In the usual apparatus was placed 150 ml of THF, 0.279 g (0.00714 g-atom) of freshly cut potassium metal. The mixture was stirred at reflux for 30 minutes. The stirring was stopped for 10 minutes at reflux until the potassium metal had coagulated on the surface of the solution. Then a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (0.90 g, 0.00227 mole) and triethylcarbinol (0.786 g, 0.00676 mole) in 15 ml of distilled THF was dumped into the mixture and the resulting mixture was stirred at reflux for 15 minutes. Upon stirring, the solution developed a light blue color. After addition of excess methanol, the mixture was transferred to a round bottom flask and the solvent was evaporated to dryness *in vacuo*. The crude mixture was diluted with some water and extracted with ether several times. After concentration of the combined ethereal extracts, a portion of the mixture was dissolved in acetone for gas chromatographic analysis.

According to the analysis, the product was found to contain 7.2% of 1-p-cyclohexylphenyl-1,1-diphenylbutane (confirmed by mixed VPC analysis with 1-p-cyclohexylphenyl-1,1-diphenylbutane isolated from reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with potassium in presence of t-butyl alcohol, see page 80), 5.5% of 1-p-biphenylyl-1,1-diphenylbutane (RH), 6.7% of 4-p-cyclohexylphenyl-1,1-diphenylbutane (confirmed by mixed VPC analysis with product from the second reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with cesium in dioxane, see page 69), 43.0% of 4-p-biphenylyl-1,1-diphenylbutane (R'H) and 37.6% of unreacted chloride based on their relative peak area percent respectively (see Table 11).

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Presence of Acetone

In the usual apparatus 150 ml of THF was distilled from sodium aluminum hydride and 0.226 g (0.0941 g-atom) of freshly cut potassium metal was introduced. After vigorous stirring at reflux for an hour, a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (0.258 g, 0.72 mmole) and acetone (0.55 g, 9.5 mmole) in 15 ml of distilled THF was dumped into the solution. The reaction mixture instantly developed a yellow color and the mixture was stirred at reflux for 2 minutes before excess methanol was added. After cooling to room temperature, the mixture was worked up as

usual to give a yellow oily material. A portion of this material in acetone solvent was subjected to gas chromatographic analysis, in which yields of products based on their relative peak area were 5.4% of 1-p-cyclohexylphenyl-1,1-diphenylbutane, 3.3% of 1-p-biphenylyl-1,1-diphenylbutane (RH), 12.4% of unknown from thermal decomposition of the unreacted chloride during the VPC analysis (assumed to be 4-p-biphenylyl-4,4-diphenyl-1-butene according to its molecular weight 360 obtained from gas chromatography-mass spectrum) and 78.9% of unreacted chloride (see Table 11).

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Presence of t-Butyl Alcohol

In run 1, into the usual apparatus for organoalkali metal reactions was placed 150 ml of freshly distilled tetrahydrofuran. To the solvent was added 0.225 g (0.00575 g-atom) of potassium free from mineral oil (potassium was melted under boiling n-heptane and separated from contaminants). The mixture was stirred vigorously at reflux for 30 minutes and cooled for 5 minutes without stirring. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.03 g, 0.00259 mole) and t-butyl alcohol (0.970 g, 0.0131 mole) in 30 ml of freshly distilled THF was dumped into the solution and the mixture was stirred with heating. After vigorous stirring at reflux for 10 minutes, 20 ml of methanol was added to the solution and the resulting mixture was continuously

Table 11. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-*p*-1,1-diphenylbutane with Potassium in Presence of Various Proton Sources

Relative Retention Time	Peak Area Percent	Identification
1. Reaction Products in *n*-Butylamine		
1.00	0.15	*p*-$PhC_6H_4CH(Ph)_2$
1.58	4.53	*p*-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.19	95.3	*p*-$PhC_6H_4(CH_2)_3CH(Ph)_2$
VPC conditions:	Column (A) temperature 260°; flow rate, 24 mm; pressure, 40 psig	
2. Reaction Products in Triethylcarbinol		
0.84	7.2	1-*p*-cyclohexylphenyl-1,1-diphenylbutane
1.00	5.5	*p*-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.12	6.7	4-*p*-cyclohexylphenyl-1,1-diphenylbutane
1.31	43.0	*p*-$PhC_6H_4(CH_2)_3CH(Ph)_2$
1.65	37.6	unreacted chloride
VPC conditions:	F&M; Column (A) temperature, 300°; flow rate, 20 mm; pressure 40 psig	
3. Reaction Products in Acetone		
0.79	5.4	1-*p*-cyclohexylphenyl-1,1-diphenylbutane
1.00	3.3	*p*-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.43	12.4	decomposed chloride in VPC
1.92	78.9	unreacted chloride
VPC conditions:	Column (A) temperature, 260°; flow rate, 20 mm; pressure 40 psig	

stirred at reflux for an additional 10 minutes until it was allowed to cool to room temperature. The mixture was worked up as usual to give a yellow solid material. A portion of this material was dissolved in acetone for the purpose of gas chromatographic analysis. The analysis indicated that it contained 9.0% of 1-p-cyclohexylphenyl-1,1-diphenylbutane, 8.2% of 1-p-biphenylyl-1,1-diphenylbutane (RH), 3.7% of 4-p-biphenylyl-4,4-diphenylbutene-1 (decomposition product from unreacted chloride during VPC analysis) and 79.1% of unreacted chloride (see Table 12).

In run 2, into 150 ml of freshly distilled THF was placed 0.223 g (0.00594 g-atom) of potassium metal (free from mineral oil) under an atmosphere of nitrogen. The mixture was stirred at reflux for 30 minutes. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.007 g, 0.00254 mole) and t-butyl alcohol (1.05 g, 0.0142 mole) in 20 ml of distilled THF was added through a dropping funnel at one time (no color change was observed). The mixture was stirred at reflux for 5 minutes until a 5 ml aliquot was hydrolyzed with methanol (Hydrocarbon I). The empty dropping funnel was filled with a solution of t-butyl alcohol (1.442 g, 0.0195 mole) in 17 ml of distilled THF. A 6 ml portion of this t-butyl alcohol in THF was added to the reaction mixture without stirring while 0.241 g (0.00614 g-atom) of oil free potassium metal was introduced to the mixture as quickly

Table 12. Gas Chromatographic Analysis of Product from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Presence of t-Butyl Alcohol (Run 1)

Relative Retention Time	Peak Area Percent	Identification
0.79	9.0	1-p-cyclohexylphenyl-1,1-diphenylbutane
1.00	8.2	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.59	3.7	p-$PhC_6H_4C(Ph)_2CHCH{=}CH_2$* (?)
1.90	79.1	unreacted chloride

VPC conditions: Column (A) temperature, 262°; flow rate, 30 mm; pressure, 40 psig

*Decomposed product of unreacted chloride during the analysis.

as possible and the mixture was stirred at reflux for 5 minutes. Stirring was stopped and a 5 ml aliquot was withdrawn to be hydrolyzed with methanol (Hydrocarbon II). To the reaction mixture was added another 6 ml portion of the solution of t-butyl alcohol in THF and 0.262 g (0.00699 g-atom) of oil-free potassium metal at the same time. Again the mixture was stirred at reflux for 5 minutes until a third 5 ml aliquot was hydrolyzed with methanol (Hydrocarbon III). The rest of the t-butyl alcohol solution (5 ml) in the dropping funnel and 0.263 g (0.00674 g-atom) of oil-free potassium metal were added to the reaction mixture and the mixture was stirred at reflux for 10 minutes. After addition of excess methanol, the mixture was cooled to room temperature and treated according to the usual work-up to give a yellow solid. A small portion of this solid was dissolved in acetone for gas chromatographic analysis (Hydrocarbon IV). The methanolysates (Hydrocarbon I, II, and III), after the usual work-up, were subjected to gas chromatographic analyses (see Table 13). Since the analytical result of "Hydrocarbon IV" still showed unreacted chloride (15.3% based on the peak area, see Table 13), the crude product was allowed to react at reflux with increments of potassium and excess t-butyl alcohol according to the following procedure. Into 150 ml of freshly distilled THF was placed 0.297 g (0.0076 g-atom) of oil free potassium metal and the solution

was stirred at reflux for 30 minutes. A solution of the crude reaction product (0.92 g) and t-butyl alcohol (1.13 g, 0.0153 mole) in 20 ml of distilled THF was dumped into the solution within a period of one second. The resulting mixture was stirred vigorously at the boiling point for 5 minutes. To the solution was added one third portion of t-butyl alcohol (1.45 g, 0.0196 mole) in 10 ml of distilled THF through a dropping funnel and immediately thereafter 0.23 g (0.00588 g-atom) of oil-free potassium metal was added without stirring. The mixture was then stirred at reflux for 5 minutes. By the same way, another one third portion of t-butyl alcohol in THF and 0.205 g (0.00525 g-atom) of oil-free potassium were added to the solution. The mixture was stirred at reflux for 5 minutes and finally the rest of t-butyl alcohol solution in the dropping funnel and 0.168 g (0.00427 g-atom) of oil-free potassium metal were introduced. The mixture was stirred vigorously at reflux for 15 minutes. After addition of excess methanol, the reaction mixture was allowed to cool to room temperature and kept overnight. The usual work-up gave a yellow viscous material. A 50 mg portion of this was saved for gas chromatographic analysis (Hydrocarbon V). According to the analysis, the reaction product (Hydrocarbon V) contained only 3.4% of 1-p-biphenylyl-1,1-diphenylbutane (RH) and give unknowns (see Table 13). One major unknown was 89.8% yield

based on the relative peak area (this was later identified as 1-p-cyclohexylphenyl-1,1-diphenylbutane from mass spectrum and nmr). Since these unknowns were believed to be Birch reduction products at that time, the reaction product was subjected to dehydrogenation. A carbon disulfide solution of 0.9 g of this reaction mixture was intimately mixed with 1 g of 5% Pd-C catalyst. The solvent was removed *in vacuo* and the mixture was heated for 5 hours on a steam bath. After dissolving the contents in 100 ml of THF, the solution was filtered. A small portion of this filtrate was directly analyzed by means of gas chromatograph (Hydrocarbon VI). According to the analysis the yield of the major unknown was not changed while that of 1-p-biphenylyl-1,1-diphenylbutane was increased to 4.37% from 3.4% and that of a minor unknown was decreased to 4.85% (see Table 13). The filtrate was removed from the solvent and the residue was subjected to another dehydrogenation reaction with 1.44 g of 5% Pd-C catalyst at 135° under a nitrogen atmosphere for 5 hours. Again the mixture was dissolved in 100 ml of THF and filtered. A small portion of this filtrate was directly subjected to gas chromatographic analysis (Hydrocarbon VII). The analysis showed that the yield of the major unknown was essentially uneffected while that of the minor unknown was decreased again from 4.85% to 2.44% while increasing the yield of unrearranged hydrocarbon (RH) from 4.37% to 6.83% (see Table

13). During the VPC analysis, the major unknown component was collected in a capillary tube and the collected sample was subjected to mass spectral analysis (see Appendix II), in which molecular ion peak was detected at 368 and base peak appeared at 325 with immense intensity. Molecular weight of the unknown has six more hydrogen units than that of 1-p-biphenylyl-1,1-diphenylbutane. This result suggested that this unknown could be either 1-p-cyclohexylphenyl-1,1-diphenylbutane or 1-(4'-phenylcyclohexyl)-1,1-diphenylbutane. Since the unknown was stable from the dehydrogenation reactions with 5% Pd-C catalyst, other possible Birch reduction products could be eliminated. By the same token the base peak at 325 would be from the stable carbonium ions either p-cyclohexylphenyldiphenylmethyl cation or (4'-phenylcyclohexyl)diphenylmethyl cation. The minor unknown which was dehydrogenated with excess of 5% Pd-C catalyst must be a 1,4-dihydroderivative of 1-p-biphenylyl-1,1-diphenylbutane. The crude reaction mixture (Hydrocarbon VII) was subjected to sublimation *in vacuo* at 130° for 4 hours to give a yellow oily material. Gas chromatographic analysis of this material showed that the relative yields of products were almost the same as that of Hydrocarbon VII. The nmr spectrum of the sublimed material was measured in CCl_4 solvent with TMS as internal standard: nmr (CCl_4), δ 7.1 (14.0 H, multiplet), 5.73 (trace H), 2.52 (2.1 H, *ca.* triplet), 2.2 (1.1 H, multi-

plet), 1.52 (16.3 H, complex multiplet), 0.92 (3.2 H, ca. triplet). According to the nmr spectrum, the crude material must be a mixture of cyclohexyl derivatives of unrearranged hydrocarbon skeleton. There was not detected the unique hydrogen peak of rearranged hydrocarbons and peaks of cyclohexyl hydrocarbons were found around δ 1.52 as a broad multiplet. Another obvious fact was that a peak corresponding to methyl hydrogens was found at δ 0.92. The UV spectrum of the sublimed material in 95% ethanol showed maxima at 260 nm. The content of triphenyl and biphenyl chromophores in the sublimed material was calculated as 88 and 12 mole percent by comparison of molar extinction coefficient of the sublimed material (ε = 2,650) with those of reference compounds, i.e., 1,1,1-triphenylethane[2] (λ_{max}^{EtOH} = 260 nm, ε = 800) and p-phenyltoluene* (λ_{max}^{EtOH} = 252.5 nm, $\varepsilon = 1.65 \times 10^3$). The remaining 0.264 g of the yellow-colored mixture (Hydrocarbon VII) was dissolved in 10 ml of distilled cyclohexane. After concentration to 3 ml, the solution was chromatographed upon a column (1.5 cm diameter and 15 cm length) packed with alumina with elution with 200 ml of cyclohexane. The eluted solution which was colorless was collected in 40 ml fractions. After dryness in vacuo, the first fraction gave 0.237 g of colorless viscous mate-

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*E. Grovenstein, Jr. and G. V. Aseff's unpublished work.

rial and the rest of three fractions yielded about 0.05 g of oily material in total. A small portion of each fraction in acetone solution were subjected to gas chromatographic analysis. The first fraction consisted of almost pure 1-*p*-cyclohexylphenyl-1,1-diphenylbutane. The colorless material (0.22 g) of the first fraction was sublimated *in vacuo* (20 μ , bath at 135°) to give 0.12 g of white crystalline solid. Recrystallization from 95% ethanol and subsequent drying *in vacuo* for 24 hours at the temperature of boiling acetone yielded 0.057 g of white crystals, mp 100.5 - 102° (new compound). A portion (0.02705 g) of these crystals was dissolved in 250 ml of 95% ethanol for determination of the UV spectrum. The spectrum had maxima at 260 mu. According to the calculated molar extinction coefficient (952), the content of biphenyl and triphenyl chromophores was estimated as 1.0 and 99.0 mole percent respectively (calculation based on the molar extinction coefficients of the same reference materials as above). The nmr spectrum was taken in CCl_4 solution [δ 7.1 (14.0 H, m), 2.52 (2.1 H, *ca*. t), 2.2 (0.9 H, broad m), 1.52 (12.2 H, m), 0.92 (2.9 H, *ca*. t)]. Since the peaks, except for the region at δ 7.1 (aromatic hydrogens), overlapped each other, the relative intensities shown above were not quite accurate; the relative ratio of the peak intensities between the aromatic hydrogens and the others was 14.0 to 18.1 (theory 14 to 18).

Anal.* Calcd. for $C_{28}H_{32}$: C, 91.24; H, 8.76.
Found: C, 91.05, 90.98; H, 8.98, 9.00.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cs-K-Na Alloy in THF at -75°

The reaction was carried out according to the procedure of Grovenstein and coworkers.[7] In the usual apparatus which were set up in a glove box under an atmosphere of nitrogen, were placed 10.6 g (0.0795 g-atom) of cesium, 3.63 g (0.0928 g-atom) of potassium and 0.562 g (0.0244 g-atom) of sodium in 250 ml of distilled THF. The mixture was stirred vigorously at reflux for one hour. Upon stirring at reflux, the solution developed a deep blue color. After cooling down to -75° in a Dry Ice-acetone bath, the solution was stirred for an additional 30 minutes. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (2.1 g, 0.0053 mole) in 20 ml of distilled THF was added over a period of 30 seconds. Upon addition of the first few drops of chloride the solution instantly developed a deep red color. The mixture was stirred for one minute until the color of the solution instantly changed to a deep green color. About one third portion of the reaction mixture was forced into water (Hydrocarbon I) and the rest of

*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Table 13. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium in Presence of t-Butyl Alchol (Run 2)

Relative Retention Time	Peak Area Percent							Identification
	Hydrocarbon Fractions							
	I	II	III	IV	V	VI	VII	
0.23	--	trace	trace	trace	trace	trace	trace	unknown
0.52	--	"	"	"	"	"	"	"
0.79	11.4	34.2	52.8	65.1	89.8	89.8	90.2	1-p-cyclohexylphenyl-1,1-diphenylbutane
1.00	3.95	12.4	17.6	14.6	3.4	4.37	6.83	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.09	1.75	3.2	4.4	5.0	5.83	4.85	2.44	1-p-(1,4-dihydrophenyl)-phenyl-1,1-diphenylbutane
1.37	--	--	--	--	0.98	0.98	0.53	unknown
1.51	1.32	0.9	trace	trace	--	--	--	p-$PhC_6H_4C(Ph)_2CH_2CH=CH_2$
1.85	81.6	49.3	25.2	15.3	--	--	--	unreacted chloride

VPC conditions: Column (B) temperature 262°; flow rate, 52 mm; pressure, 40 psig

the mixture was forced onto crushed solid carbon dioxide with a nitrogen stream. The carbonated mixture was worked up as usual to give 0.504 g of neutral material (Hydrocarbon II) and 0.94 g of acidic material. A portion of the acid (20 mg) was converted to methyl esters by reaction with diazomethane prior to analysis by gas chromatography; this analysis showed only two components, 4.6% of unknown and 95.4% of the ester of the rearranged acid but none of the unrearranged acid. The identity of the rearranged acid was confirmed by mixed gas chromatography with an authentic sample. One recrystallization of the acid (0.62 g) from glacial acetic acid gave 0.47 g of white crystals, mp 187.4 - 189.2°. After further recrystallization from glacial acetic acid and n-pentane, the acid was dried *in vacuo* at 58° for overnight to give 0.33 g of nearly pure crystals, mp 190 - 191.2°, which was identified as 5-p-biphenylyl-2,2-diphenylpentanoic acid by nmr spectrum and mixture melting point; nmr (CCl_4); δ 7.25 (19.0 H, broad multiplet, aromatic hydrogens), 2.50 (4.1 H, complex multiplet attributed to overlapping triplets, methylene groups next to biphenylyl and carboxylic groups), 1.45 (2.1 H, complex multiplet, central methylene group). The usual work-up of the hydrolysate gave 0.61 g of crude hydrocarbon. Small portions of Hydrocarbons I and II were prepared for gas chromatographic analyses (see Table 14). According to the analyses, both Hydrocarbon I and II showed five components

in which two components were identified as p-biphenylyldiphenylmethane and 4-p-biphenylyl-1,1-diphenylbutane (R'H) and the remaining three components were unknowns (see Table 14). Since these unknowns were believed to be Birch-reduction products, Hydrocarbon I was subjected to a dehydrogenation procedure. A carbon disulfide solution of 0.6 g portion of the Hydrocarbon I was mixed with 1 g of 5% Pd-C catalyst. After evaporation to dryness in vacuo, the mixture was heated at 125° for 20 hours under an atmosphere of nitrogen. The mixture was dissolved in hot acetone and the solution was filtered. Gas chromatographic analysis of a portion of the filtrate (Hydrocarbon III) indicated that the relative yield of three unknowns decreased while that of two knowns increased as shown in Table 14. The filtrate was evaporated to dryness again in vacuo and again the hydrocarbon was dehydrogenated under the same conditions as above for 20 hours until a portion of the mixture was analyzed by gas chromatography (Hydrocarbon IV). The rest of the reaction mixture was subjected to dehydrogenation for an addition 32 hours under the same conditions. After dissolving in the hot-acetone, the solution was filtered. Gas chromatographic analysis of a portion of the filtrate (Hydrocarbon V) clearly indicated that the three unknowns were Birch-reduction products (see Table 14).

Table 14. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cs-K-Na Alloy in THF at -75°

Relative Retention Time	Peak Area Percent					Identification
1. Neutral Materials	Hydrocarbon Fractions I	II	III	IV	V	
0.82	2.1	0.65	0.37	0.21	--	unknown (p-cyclohexyltriphenylmethane?)
1.00	4.4	16.7	8.21	8.27	8.68	p-$PhC_6H_4CH(Ph)_2$
1.21	2.1	2.9	0.28	0.34	--	unknown (Compound B?)*
1.53	--	--	2.6	2.78	2.77	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$*
1.74	15.1	3.44	6.65	4.97	3.23	unknown (Compound C?)*
2.21	76.3	76.3	81.9	83.4	85.3	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2. Acidic Materials as Methyl Esters						
1.77	4.6					unknown
3.62	95.4					p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$

VPC conditions: Column (A) temperature, 260°, flow rate, 22 mm; pressure, 40 psig

*Structures are given in Appendix II.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75°

Into 300 ml of freshly distilled tetrahydrofurn was placed lithium metal (1.88 g, 0.271 g-atom) in small pieces. Approximately five percent of solution of 0.382 g (0.00248 mole) of biphenyl in 20 ml of distilled THF and 1 ml (0.016 mole of methyl iodide were added to the solution. Then the solution was stirred vigorously for 40 minutes at room temperature until the solution developed a deep green color. When the solution was cooled down to -75°, the color changed to a deep blue. To the solution was added the rest of the biphenyl in THF over a period of 5 minutes. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.99 g, 0.00502 mole) in 20 ml of distilled THF was added dropwise to the solution with vigorous stirring. Upon addition of one third of the chloride over a period of one and one-half minutes, the blue color disappeared. Then the addition of the chloride was stopped and the solution was stirred vigorously to develop the blue color but a brown color appeared in 3 minutes instead of the blue. After 5 minutes stirring the brown color turned to a black brown. To the solution was added the rest of the chloride in dropping funnel over a period of 15 minutes with vigorous stirring. The color of the solution did not change during this addition. The reaction mixture was stirred at -75° for an additional 10 minutes until it

was siphoned onto solid carbon dioxide through a glass tube fitted with a fine mesh screen of stainless steel on one end (to remove excess lithium). Methyl alcohol was added to the residual reaction mixture in the flask and the flask was kept overnight. Next day the mixture in the flask was extracted with ether and the extract dried over anhydrous $MgSO_4$. The ether was then removed in vacuo and the residue was dissolved in acetone for gas chromatographic analysis (Hydrocarbon I). The carbonated mixture was concentrated to dryness in vacuo and aqueous NaOH solution was added to the residue. The mixture was extracted with ether to yield 1.24 g (included biphenyl) of neutral material (Hydrocarbon II). The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether to give 0.907 g of acidic material. A small portion of the acid was transformed to methyl ester. This acid ester was analyzed quantitatively by comparison with authentic acid esters (rearranged and unrearranged acid esters) upon gas chromatograpy. According to the analysis at least 91.5% of the acids formed volatile (two small unknowns were not included, see Table 15). Since Hydrocarbon I was kept overnight with excess lithium metal in the presence of proton donors before it was analyzed by gas chromatography, the analysis showed more complex products than those of the Hydrocarbon II. Obviously some of the products in Hydrocarbon I were formed by further re-

Table 15. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 1)

Relative Retention Time	Peak Area Percent (Abs. Yield Mg, Mole % Yield)		Identification
1. Neutral Materials	Hydrogen Fraction I	II	
0.80	0.78		unknown
1.00	7.77	5.6 (23.4, 1.45%)	p-$PhC_6H_4CH(Ph)_2$
1.17	5.88		1-(p-cyclohexylphenyl)-1,1-diphenylbutane
1.48		11.9 (49.8, 2.72%)*	unknown
1.54	61.6	65.3 (274, 15.0%)	p-$PhC_6H_4(Ph)_2(CH_2)_3H$
2.11	12.2	17.2 (72, 3.97%)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.37	11.8		4-p-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane (?)

VPC conditions: Column (A) temperature, 262°; flow rate, 22 mm; pressure, 40 psig

Table 15. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 1) (Continued)

Relative Retention Time	Peak Area Percent (Abs. Yield Mg, Mole % Yield)	Identification
2. Acidic Materials as Methyl Esters		
0.43	0.78	unknown
0.48	1.81	unknown
1.00	26.1 (222, 10.9%)	p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.11	71.3 (607, 29.7%)	p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$

VPC conditions: Column (B) temperature, 256°; flow rate, 21 mm; pressure, 40 psig

*Calculations based on use of p-$PhC_6H_4(Ph)_2(CH_2)_3H$ for calibration factor.

duction with lithium metal (see Table 15). Quantitative gas chromatographic analysis of Hydrocarbon II showed its volatile component to be about 34% by the crude weight (biphenyl and its derivatives which had very short retention times under the VPC conditions are not included in the Table).

In run 2, 300 ml of freshly distilled tetrahydrofuran and 0.36 g (0.052 g-atom) of lithium metal cut into small pieces were placed in the usual apparatus under an atmosphere of nitrogen. Into the solution were introduced 6.2 g (0.0404 mole) of biphenyl and 1 ml (0.016 mole) of methyl iodide. The mixture was stirred vigorously at room temperature for 10 minutes until the solution developed a deep blue color. After cooling down to -75° the mixture was stirred vigorously for an additional 2 hours. During the stirring at this temperature, no color change was observed. A solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.99 g, 0.00591 mole) in 44 ml of distilled THF was added dropwise over a period of 15 minutes. At the end of the addition of the chloride, the color of the solution slowly turned blue-green. Then the stirring was stopped immediately and the reaction mixture was siphoned onto crushed solid carbon dioxide through the usual glass tube fitted with a filter screen. To the small residue in the flask was added excess methanol to decompose excess lithium and the mixture was kept overnight. After the usual work-up, the methanolysate

was subjected to gas chromatographic analysis (see Hydrocarbon III of Table 16). The carbonated mixture was worked up as usual to give 7.23 g of neutral material (Hydrocarbon IV, including biphenyl and its derivatives) and 0.26 g of acidic material. Gas chromatographic analysis of a portion of the Hydrocarbon IV revealed the relative ratio of RH to R'H as 84.8 to 15.2 (see Table 16). If unreacted chloride were present in product during the gas chromatographic analysis, usually the chloride would be partially decomposed to an olefin which has a slightly longer retention time than that of the rearranged hydrocarbon but the two peaks usually overlapped to give one peak due to the broadness. Since both Hydrocarbons I and II contained unreacted chloride, the actual peak area percent of the rearranged hydrocarbons in Table 16 was evaluated on the assumption that the fraction of chloride decomposed was the same as in a sample of pure chloride run under the same conditions. A portion of the acid was transformed to its methyl ester before it was analyzed by gas chromatography. The analysis of the acid ester showed negligible amount of unrearranged acid ester with two unknowns (see Table 16).

In run 3, into 250 ml of freshly distilled tetrahydrofuran were introduced 0.68 g (0.098 g-atom) of lithium cut into small pieces and 1 ml (0.016 mole) of methyl iodide and the mixture was stirred at room temperature for 5 minutes to activate the lithium. To the mixture was added

Table 16. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 2)

Relative Retention Time	Peak Area Percent (Relative Ratio: RH to R'H)			Identification
1. Neutral Materials	Hydrocarbon Fractions III	IV	Auth. RCl*	
0.84	1.19			unknown
1.00	10.7	7.48		p-$PhC_6H_4CH(Ph)_2$
1.18	2.38			1-p-cyclohexylphenyl-1,1-diphenylbutane
1.35	2.98	4.19		unknown
1.47	53.4 (82.9)	43.1 (84.8)		p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.97	11.0 (17.1)	7.7 (15.2)		p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.27	2.81	5.76	15.3	p-$PhC_6H_4C(Ph)_2CH_2CH=CH_2$
2.61	15.5	31.8	84.7	unreacted chloride

Table 16. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 2) (Continued)

Relative Retention Time	Peak Area Percent (Relative Ratio: RH to R'H)	Identification
2. Acidic Materials as Methyl Esters		
1.63	100	unknown
2.72	trace	unknown
3.08	trace	p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$

VPC conditions: Column (B) temperature, 276°;

flow rate, 30 mm; pressure, 40 psig

*Behavior of authentic chloride under the VPC conditions.

a solution of 7.73 g (0.0502 mole) of biphenyl in 50 ml of distilled THF. The well stirred mixture developed a deep blue color within 2 minutes. After cooling down to -75°, the mixture was continuously stirred for 3 hours. A solution of 0.274 g (0.00297 mole) of n-BuCl in 10 ml of distilled THF was added to the mixture as a drying agent over a period of 5 minutes followed by 5 minutes of stirring. To the mixture was added a solution of 4-chloro-1-p-biphenyl-1,1-diphenylbutane (1.00 g, 0.00252 mole) in 20 ml of distilled THF over a period of 40 minutes under the continuous stirring. At the end of the addition of the chloride, the color of the solution was slightly lightened but it was still deep blue (careful observation could detect a green coloration in the solution). The reaction mixture was stirred vigorously for an additional 5 minutes before it was siphoned onto crushed solid carbon dioxide by means of a nitrogen stream (excess lithium was removed). The usual work-up yielded 7.83 g of neutral material (included biphenyl and its derivatives) and 0.604 g of acidic material. Quantitative gas chromatographic analysis of the neutral material from carbonation yielded 10.6% of p-biphenylyldiphenylmethane, 41.5% of 1-p-biphenylyl-1,1-diphenylbutane (RH) and 0.93% of 4-p-biphenylyl-1,1-diphenylbutane (R'H) based on the chloride used in the reaction (see Hydrocarbon I of Table 17). A small portion of the acid was transformed

Table 17. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 3)

Relative Retention Time	Peak Area Percent [Abs. Yield mg, mmole] (Relative Ratio)		Identification
1. Neutral Materials		2.*	
1.00	19.6 [85.2, 0.266]	10.2 [85, 0.266]	p-$PhC_6H_4CH(Ph)_2$
1.56	78.6 [379, 1.41] (97.8%)	85.0 [707, 1.95] (94.6%)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.22	1.8 [8.3, 0.023] (2.2%)	4.8 [40, 0.11] (5.4%)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
VPC conditions: Column (A) temperature, 260°; flow rate, 21 mm; pressure, 40 psig			
3. Acidic Materials as Methyl Esters			
0.42	1.09		unknown
0.46	5.76		unknown
1.00	8.95 [35.4, 0.087] (9.6%)		p-$PhC_6H_4(CH_2)_3(Ph)_2CO_2H$
1.14	84.2 [333, 0.82] (90.4%)		p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$
VPC conditions: Column (A) temperature, 250°; flow rate, 23 mm; pressure, 40 psig			

*Calculated yield of hydrocarbons if the reaction mixture were hydrolyzed.

to its methyl ester prior to gas chromatographic analysis. According to the quantitative analysis, the acid was found to contain 3.46% of rearranged acid and 32.5% of unrearranged acid based on the chloride used (see Table 17). Calculations (which were made for comparison with other runs) showed that if the reaction mixture had been hydrolyzed instead of carbonated, the relative weight ratio of the hydrocarbons would be 10.2% of p-biphenylyldiphenylmethane, 85% of unrearranged hydrocarbon (RH) and 4.8% of rearranged hydrocarbon (see Hydrocarbon 2 of Table 17).

In run 4, two sets of the usual apparatus were arranged side by side so that solution could be siphoned from one flask into the other without being exposed to the atmosphere and the apparatus was kept under an atmosphere of nitrogen. Into the first flask were placed 350 ml of freshly distilled THF and 0.698 g (0.101 g-atom) of lithium cut into small pieces. After introducing 1 ml (0.016 mole) of methyl iodide, the solution was stirred vigorously for 10 minutes at room temperature until 29.7 g (0.193 mole) of biphenyl was dumped into the solution within one second. Upon stirring for 7 minutes at room temperature, the solution developed instantly a deep blue color and then the mixture was cooled down to -75° as quickly as possible. After stirring vigorously for 30 minutes, a solution of 0.233 g (0.00252 mole) n-BuCl in 10 ml of distilled THF

was introduced to the mixture by injection with a hypodermic syringe. The blue color of the mixture disappeared for a second when the chloride was added but the color reappeared immediately as the stirring was continued. The mixture was kept under vigorous stirring for an additional three and one-half hours at the low temperature until the mixture was siphoned into the other flask to remove unreacted lithium. To the residual mixture (50 ml) in the flask was added excess methanol to decompose the unreacted lithium metal. After cooling down the siphoned mixture to -75°, another solution of n-BuCl (0.221 g, 0.00239 mole) in 10 ml of distilled THF was added to the mixture over a period of 5 minutes while the mixture was under vigorous stirring. To the mixture was then added over a period of 15 minutes with continuous stirring a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.01 g, 0.00252 mole) in 15 ml of distilled THF. During the addition of the both chlorides no color change was observed. The reaction mixture was stirred for an additional 5 minutes until it was carbonated. To the small residue in the flask was added methanol. After concentration, the methanolysate was extracted with ether and the extract was prepared for gas chromatographic analysis (Hydrocarbon V), in which unrearranged hydrocarbon was found as a major product and a trace amount of rearranged hydrocarbon was detected (see Table 18). The usual work-up on

Table 18. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 4)

Relative Retention Time	Peak Area Percent (Rel. wt. %) [Abs. yield g, mol% yield]			Identification
1. Neutral Materials	Hydrocarbon Fraction V		VI	
1.00	15.7 (14.4)	27.6 (25.6)	[0.0784, 9.72]	p-$PhC_6H_4CH(Ph)_2$
1.08		4.4 (4.1)	[0.0125, 1.54]	p-(1,4-dihydrophenyl)-phenyldiphenylmethane(?)
1.54	84.3 (85.6)	68.0 (70.3)	[0.215, 23.6]	p-$PhC_6H_4C(Ph)_2(CH_2)_3$
2.22	trace*			p-$PhC_6H_4(CH_2)_3CH(Ph)_2$

VPC conditions: Column (A) temperature, 260°;

flow rate, 20 mm; pressure, 40 psig

Table 18. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 4) (Continued)

Relative Retention Time	Peak Area Percent (Rel. wt. %) [Abs. yield g, mol% yield]	Identification
2. Acidic Materials as Methyl Esters		
0.12 >	unmeasurable	at least 6 unknowns
0.49	3.88	unknown
1.00	3.16 [0.019, 1.86]	p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.13	93.0 [0.555, 53.9]	p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$

VPC conditions: Column (A) temperature, 258°;

flow rate, 12 mm; pressure, 40 psig

*Less than 0.01 percent.

the carbonated mixture yielded 24.9 g of neutral material (Hydrocarbon VI, included biphenyl and its derivatives) and 0.91 g of acidic material. Quantitative gas chromatographic analysis of Hydrocarbon VI gave 0.0784 g of p-biphenylyldiphenylmethane, 0.0125 g of p-(1,4-dihydrophenyl)phenyldiphenylmethane (?) and 0.215 g of 1-p-biphenylyl-1,1-diphenylbutane but rearranged hydrocarbon was not detected in the analysis (see Table 18). Quantitative gas chromatographic analysis of the acid (as methyl ester) gave a 3.3 to 96.7 ratio of rearranged to unrearranged acid (see Table 18).

In run 5, each of two Morton flasks (3 and 2-l by volume) equipped with a dropping funnel, a Vigreux column and a high-speed stirrer were set up side by side as indicated in the previous run and were dried with a flame under a stream of nitrogen. Into the 3-l flask were placed 1150 ml of freshly distilled tetrahydrofuran and 0.803 g (0.116 g-atom) of lithium. After addition of 1 ml (0.016 mole) of methyl iodide, the solution was stirred for ten minutes at room temperature. Into the mixture was introduced 6.29 g (0.0409 mole) of biphenyl and the solution was stirred vigorously at the same temperature. After stirring for 50 minutes, the mixture was developed instantly a deep blue color and was stirred for an additional 10 minutes. The temperature was then lowered to -75° and the solution was kept under vigorous stirring for 4 hours until 1100 ml of

the mixture was siphoned into the second flask through a filter tube to remove excess lithium metal. The mixture in the second flask was kept at -75° for 75 minutes until the amount of lithium biphenyl was estimated from a Gilman titration. In this analysis six 10 ml aliquots were withdrawn and three of the aliquots were hydrolyzed by adding to 10 ml of water and the remainder were decomposed with 5 ml of distilled benzyl chloride followed by 5 ml of water and then all were titrated with standard hydrochloric acid with the use of phenolphthalein as an indicator. The amount of lithium biphenyl in the solution was found to be 0.018 mole from the triple titrations. Upon stirring the mixture, a solution of 0.237 g (0.00257 mole) of n-BuCl in 10 ml of distilled THF was added dropwise over a period of 10 minutes (no color change was observed) and then 1.008 g (0.00254 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 25 ml of distilled THF was added over a period of 15 minutes. At the end of the addition of the chloride, the color of the solution had changed to a green-blue. The reaction mixture was stirred for an additional 5 minutes until it was forced onto crushed solid carbon dioxide. To the small residue in the flask was added methanol (Hydrocarbon VII). After the usual work-up, gas chromatographic analysis of the methanolysate (Hydrocarbon VII) gave 87.9 to 12.1 ratio of unrearranged to rearranged hydrocarbon

(see Table 19). The usual work-up on the carbonated material yielded 6.55 g of neutral material (Hydrocarbon VIII) and 0.411 g of crude acidic material. According to the quantitative gas chromatographic analysis, the hydrocarbon VIII was found to contain only 0.325 g of volatile components and gave an 81 to 19 ratio of unrearranged to rearranged hydrocarbon (see Table 19). Quantitative gas chromatographic analysis of the acid (as methyl ester) gave a 3.9 (0.0022 g) to 96.1 (0.054 g) ratio of rearranged to unrearranged acid among the several unknowns (see Table 19). According to the analyses, the total yield of the volatile known compounds was 44.2 mole % based on the chloride used and the rest was thought to be decomposed and polymerized products. Since the analysis of the acid ester showed that one unknown component (Compound E) contributed 30.1 percent to the total volatile components (based on the relative peak area), the acid was subjected to nmr spectroscopy in carbon tetrachloride solvent to probe the structure of unknown (see Appendix I).

In run 6, two 500 ml Morton flasks equipped in the usual manner were set up side by side and dried with flame under a stream of nitrogen. Into the first flask was placed 300 ml of freshly distilled tetrahydrofuran and 0.701 g (0.101 g-atom) of lithium under an atmosphere of nitrogen. One ml (0.016 mole) methyl iodide was then added with vigor-

Table 19. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 5)

Relative Retention Time	Peak Area Percent (Rel. wt. %) [Abs. Yield g, mol% Yield]		Identification
1. Neutral Materials	Hydrocarbon Fraction VII	VIII	
1.00	4.0 (3.64)	18.9 (17.2) [0.056, 6.89]	p-$PhC_6H_4CH(Ph)_2$
1.46	84.4 (84.7)	65.7 (67.1) [0.218, 23.7]	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.05	11.6 (11.7)	15.4 (15.7) [0.051, 5.55]	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
VPC conditions: Column (A) temperature, 262°; flow rate, 14 mm, pressure, 40 psig			
2. Acidic Materials as Methyl Esters			
0.11>	unmeasurable		several unknowns
0.28	3.48		unknown
0.49	4.23		unknown
0.85	30.1 [0.027, 2.61]		Compound E*
1.00	2.43 [0.0022, 0.21]		p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.09	59.7 [0.054, 5.24]		p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$
VPC conditions: Column (A) temperature, 252°; flow rate, 15 mm; pressure, 40 psig			

*See Appendix I

ous stirring at room temperature. After stirring 10 minutes 29.4 g (0.191 mole) of biphenyl was introduced into the solution and the mixture was stirred vigorously. A deep blue color appeared within two minutes and the mixture was kept under vigorous stirring for an additional 5 minutes at room temperature until it was cooled down to -75°. After the vigorous stirring for 4 hours at -75°, 260 ml of the reaction mixture was transferred to the second flask through a glass siphon tube designed to remove excess lithium and the mixture was kept at -75°. Double Gilman titration (upon 20 ml of the solution) indicated the amount of lithium biphenyl to be 0.062 mole in the remaining 240 ml of solution. On stirring the mixture, a solution of 0.22 g (0.0024 mole) of n-BuCl in 10 ml of distilled THF was added to the mixture over a period of 10 minutes and immediately thereafter was added a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (0.99 g, 0.0025 mole) in 20 ml of distilled THF over a period of 15 minutes. During the addition of the both chlorides, no color change was observed in the solution. The mixture was stirred for an additional 5 minutes until it was forced onto crushed solid carbon dioxide and methanol was added to the small residue in the flask (Hydrocarbon IX). Gas chromatographic analysis of Hydrocarbon IX revealed a 97.9 to 2.1 ratio of unrearranged to rearranged hydrocarbon (see Table 20). The carbonated material was worked up as usual to give 23.1 g of crude

Table 20. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 6)

Relative Retention Time	Peak Area Percent (Rel. wt. %) [Abs. Yield g, mol % Yield]		Identification
1. Neutral Materials	Hydrocarbon Fractions IX	X	
1.00	5.68 (5.16)	31.6 (29.3) [0.102, 12.8]	p-$PhC_6H_4CH(Ph)_2$
1.53	92.4 (92.9)	65.6 (67.8) [0.236, 26.1]	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.11	1.94 (1.95)	2.79 (2.87) [0.01, 1.1]	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
VPC conditions: Column (A) temperature, 262°; flow rate, 15 mm; pressure, 40 psig			
2. Acidic Materials as Methyl Esters			
0.11 >	unmeasurable		several unknowns
0.49	3.78		unknown
1.00	2.35 [0.0099, 0.98]		p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.13	93.9 [0.394, 38.8]		p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$
VPC conditions: Column (A) temperature, 253°; flow rate, 12 mm; pressure, 40 psig			

neutral material (Hydrocarbon X) and 0.701 g of brown-oily acid. Hydrocarbon X was found to contain 0.348 g of volatile compounds from a quantitative gas chromatographic analysis and the ratio of unrearranged to rearranged hydrocarbon was 95.9 to 4.1 (see Table 20). The acid was analyzed quantitatively (as methyl esters) by gas chromatography to give a 2.4 to 97.6 ratio of rearranged to unrearranged acid (see Table 20). The known volatile components in both products amounted 79.8 mole percent based on the chloride used.

In run 7, the usual apparatus were set up as in the previous runs. Into the first flask were placed 300 ml of freshly distilled tetrahydrofuran and 0.701 g (0.101 g-atom) of lithium. The solution, after addition of 1 ml (0.016 mole) methyl iodide, was stirred vigorously for 10 minutes at room temperature until 7.71 g (0.050 mole) of biphenyl was dumped into the solution. Upon stirring the solution developed a deep blue color within two minutes and the mixture was thereupon cooled down to -75° as quickly as possible. Then the mixture was kept under vigorous stirring for 4 hours until about 260 ml of the reaction mixture was siphoned into the second flask to remove excess lithium and the mixture was kept at -75° without stirring for 40 minutes. The amount of lithium biphenyl was found to be 0.0126 mole in the remaining 250 ml of reaction mixture from Gilman titration. Upon stirring the mixture, a solution of n-BuCl

(0.219 g, 0.00237 mole) in 10 ml of distilled THF was added over a period of 3 minutes (no color change was observed) and then 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (0.956 g, 0.00241 mole) in 20 ml of distilled THF was added over a period of 5 minutes. Upon the addition of the latter chloride, the color of the solution gradually changed to a green-blue and when the stirring was stopped, a pink color developed in the solution within one minute. The reaction mixture was carbonated as usual and the small residue (30 ml) in the flask was hydrolyzed with methanol (Hydrocarbon XI). After the usual work-up, the carbonated mixture yielded 5.91 g of crude neutral material (Hydrocarbon XII) and 0.842 g of acidic material. Gas chromatographic analysis of Hydrocarbon XI gave 91.7 to 8.3 ratio of unrearranged to rearranged hydrocarbon and the ratio of the former to the latter hydrocarbon in the Hydrocarbon XII was found to be 95.7 to 4.3 from quantitative gas chromatographic analysis (see Table 21). Quantitative VPC analysis of the acid (as methyl ester) is given in Table 21. According to the quantitative VPC analyses of the products, the known volatile compounds were formed in 73.4 percent yield based on the chloride used.

Reaction of Neophyl Chloride with Lithium Biphenyl in THF at -75°

In run 1, the usual apparatus for organoalkali

Table 21. Gas Chromatographic Analyses of Products from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 7)

Relative Retention Time	Peak Area Percent (Abs. Yield mg, Mole % Yield)			Identification
1. Neutral Materials	Hydrocarbon Fraction XI		XII	
1.00	trace	1.76	(0.65, 0.084)	p-$PhC_6H_4CH(Ph)_2$
1.43	89.5	62.8	(25.7, 2.95)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.95	8.14	2.82	(1.16, 0.13)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.01		7.05	(18.2, 2.01)	p-$PhC_6H_4C(Ph)_2CH_2CH{=}CH_2$*
2.65	2.39	25.6		unreacted chloride
VPC conditions: Column (A) temperature, 262°; flow rate, 16 mm; pressure, 40 psig				
2. Acidic Materials as Methyl Esters				
1.00	7.5 (50, 5.11)			p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.12	92.5 (618, 63.1)			p-$PhC_6H_4C(Ph)_2(CH_2)_3CO_2H$
VPC conditions: Column (A) temperature, 255°; flow rate, 17 mm; pressure, 40 psig				

*Decomposed product from unreacted chloride during the analysis

metal reactions were set up, dried with flame and kept under an atmosphere of nitrogen. Into the 500 ml Morton flask were placed 300 ml of freshly distilled tetrahydrofuran and 1.23 g (0.177 g-atom) of lithium cut into small pieces. After introducing 1 ml (0.016 mole) of methyl iodide, the solution was stirred vigorously for 5 minutes at room temperature. Then a solution of biphenyl (26.3 g, 0.171 mole) in 50 ml of distilled THF was dumped into the solution through a dropping funnel while the solution was continuously stirred. About 5 minutes later, the solution instantly developed a deep blue color and was cooled down to -75°. The solution was kept under vigorous stirring for 3 hours at the low temperature while no further color change was observed. To the solution was added a solution of neophyl chloride (5.61 g, 0.0333 mole) in 20 ml of distilled THF over a period of 80 minutes. Until half of the chloride had been added, the solution did not show any color change but after this time careful observation could detect momentary yellow globules at the surface of the solution around the side neck of the flask when drops of the chloride solution come in contact with the reaction mixture. These yellow globules disappeared immediately when the mixture was sufficiently stirred. The color of the solution gradually turned to a deep blue-green when two thirds of the chloride was added and was almost green at the end of the addition. The

mixture was kept under vigorous stirring for an additional 15 minutes. Then the stirring was stopped and the mixture was forced onto the crushed solid carbon dioxide. The usual work-up yielded 28.5 g of crude neutral material and 4.53 g of crude acid. According to the quantitative gas chromatographic analyses the neutral material was found to contain 0.213 g of t-butylbenzene and 0.929 g of unreacted neophyl chloride and the acid (as methyl ester) gave 4.52 g of unrearranged acid and 0.054 g of rearranged acid (see Table 22).

In run 2, lithium biphenyl was prepared from the reaction of 1.23 g (0.177 g-atom) of lithium with 19.9 g (0.129 mole) of biphenyl in 350 ml of freshly distilled tetrahydrofuran at -75° for two hours and 30 minutes. Then a solution of neophyl chloride (6.2 g, 0.0368 mole) in 40 ml of distilled THF was added dropwise with vigorous stirring over a period of 25 minutes. After two fifths of the chloride was added, the color of the reaction mixture changed to green and gradually turned mustard yellow on continued addition of the chloride. The reaction mixture was stirred vigorously for an additional three hours at -75° until it was carbonated. The usual work-up on the carbonated mixture yielded 23.1 g of crude neutral material and 3.14 g of crude acid. Quantitative gas chromatographic analysis showed that the neutral material contained 1.46 g of t-butylbenzene, 1.73 g of unreacted chloride and about 0.9 g of

Table 22. Gas Chromatographic Analyses of Products from Reaction of Neophyl Chloride with Lithium Biphenyl in THF at -75° (Run 1 and 2)

Relative Retention Time	Peak Area Percent (Abs. yield g, mole % Yield)		Identification
1. Neutral Materials	Run 1	Run 2	
1.00	23.6 (0.213, 4.78)	40.3 (1.46, 29.6)	$C_6H_5C(CH_3)_3$
1.36	1.04	24.8	unknown
2.64	75.4 (0.929, 16.6)	34.9 (1.73, 27.9)	$C_6H_5C(CH_3)_2CH_2Cl$
4.61	not determined	not determined	$C_6H_5-C_6H_5$
VPC conditions: F&M 810; 10% Apiezon L (6 ft); column temperature, 148°; flow rate, 17 mm; pressure, 40 psig			
2. Acidic Materials as Methyl Esters			
1.00	1.2 (0.055, 0.93)	1 (0.02, 0.31)	$C_6H_5CH_2C(CH_3)_2CO_2H$
1.14	98.8 (4.47, 75.5)	99 (2.07, 31.6)	$C_6H_5C(CH_3)_2CH_2CO_2H$
VPC conditions: F&M 810; 10% Apiezon L (6 ft); column temperature, 148°; flow rate, 20 mm; pressure, 40 psig			

unknown (calculation based on the t-butylbenzene) which has longer retention time than neophyl chloride. The acid (as methyl ester) was found to contain 2.07 g of unrearranged acid and 0.02 g of rearranged acid (2,2-dimethyl-3-phenylpropanoic acid) from a quantitative VPC analysis (see Table 22).

Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Potassium t-Butoxide in THF at -75°

In run 1, two sets of the usual apparatus were arranged side by side so that the solution from the first flask could be siphoned into the second under a stream of nitrogen. Into the first flask were placed 300 ml of freshly distilled THF and 9.51 g (0.243 g-atom) of freshly cut potassium metal under an atmosphere of nitrogen. The solution was held at reflux with high-speed stirring for 10 minutes and then a solution of t-butyl alcohol (8.86 g, 0.12 mole) in 10 ml of distilled THF was added over a period of 20 minutes. After vigorous stirring at reflux for 30 minutes, the stirring was stopped and the solution was allowed to cool down to room temperature so that the unreacted potassium metal would coagulate to large clusters (the mixture was heated to reflux temperature and cooled down to room temperature several times with occasional slow stirring until the potassium metal coagulated). Then the clear solution was kept standing at room temperature for two hours

under an atmosphere of nitrogen and finally was cooled down to -75°. Into the second flask 250 ml of freshly distilled tetrahydrofuran and 1.55 g (0.223 g-atom) of lithium cut into small pieces were introduced. After addition of 0.1 ml (0.0016 mole) of methyl iodide the solution was stirred vigorously for 10 minutes at room temperature and then cooled down to -75°. To the mixture was added a solution of n-BuCl (0.97 g, 0.0105 mole) in 15 ml of distilled THF over a period of 20 minutes. Next a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.01 g, 0.00255 mole) in 25 ml of distilled THF was added over a period of 25 minutes. Upon the addition of the latter chloride, the solution instantly developed a pale orange-pink color, which was gradually deepened to a dark pink with continuous stirring. The reaction mixture was kept under a vigorous stirring for an additional 90 minutes at -75° until a green-black color appeared in the solution. Five ml aliquot of the reaction mixture was hydrolyzed with methanol for gas chromatographic analysis (Hydrocarbon I). To the rest of the reaction mixture in the second flask was transferred about 150 ml of the potassium t-butoxide solution from the first flask (freed from potassium metal by filtration through a glass siphon tube covered at one end with a fine-meshed stainless steel screen). The color of the solution instantly deepened to a dark pink color and the mixture was stirred for 20 seconds for well mixing.

The resulting solution was then kept standing at -75° without stirring until decomposition. Gas chromatographic analysis of Hydrocarbon I showed 52.5 to 47.5 ratio of unrearranged (RH) to rearranged hydrocarbon (R'H). After standing for one hour, a 5 ml aliquot of the reaction mixture was hydrolyzed with methanol (Hydrocarbon II) and the VPC analysis of the methanolysate (Hydrocarbon II) gave 25.3 to 74.7 ratio of unrearranged (RH) to rearranged hydrocarbon (R'H). On standing for two hours, another 5 ml of the mixture was withdrawn to hydrolyze with methanol (Hydrocarbon III) and the VPC analysis of the Hydrocarbon III revealed an almost identical the ratio of unrearranged to rearranged hydrocarbon to that of the Hydrocarbon II (25.7 to 74.3). The reaction mixture was finally kept for 3 hours at -75° under the nitrogen atmosphere until a portion of 5 ml of the mixture was hydrolyzed with methanol (Hydrocarbon IV) and the reaminder forced onto the crushed solid carbon dioxide. According to the gas chromatographic analysis, Hydrocarbon IV (whose ratio of unrearranged to rearranged hydrocarbon was 24.4 to 75.6) was essentially of the same composition as Hydrocarbons II and III. The carbonated mixture, after concentration, was acidified with aqueous hydrochloric acid solution and extracted with ether. The acids in the ethereal ether extract was separated from the neutral compounds by washing with aqueous potassium hydroxide solution several times. The usual work-up of the neutral

fraction yielded 0.284 g of crude material (Hydrocarbon V). After acidification of the potassium salts with concentrated hydrochloric acid, the resulting acids were extracted with ether and the usual work-up on the ethereal solution gave 0.573 g of acid. According to quantitative gas chromatographic analysis, Hydrocarbon V gave an 80.4 to 19.6 ratio of unrearranged to rearranged hydrocarbon and the acid fraction (as methyl esters) were found to contain 0.55 g of rearranged acid (53 mole percent yield based on the chloride used) but no unrearranged acid could be detected (relative retention time 1.07, see Table 23). One notable fact was that the acid fraction (as lithium salts) in the carbonated mixture was not separated from the neutral fraction when the aqueous carbonated mixture was extracted with ether. The separated ethereal phase was found to contain most of the both fractions and the separated aqueous phase, after the usual work-up, gave only a tiny amount of the rearranged acid with several unknowns (i.e., 0.03 g of the rearranged acid was obtained from the aqueous solution according to the quantitative VPC analysis).

In run 2, potassium t-butoxide was prepared in 300 ml of freshly distilled tetrahydrofuran from the reaction of 9.53 g (0.244 g-atom) of potassium metal with 8.9 g (0.12 mole) of t-butyl alcohol, the latter added at reflux temperature over a period of 30 minutes; the solution was then held at reflux with vigorous stirring for an additional

Table 23. Gas Chromatographic Analyses of Products from Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Potassium t-Butoxide in THF at -75° (Run 1)

Relative Retention Time	Peak Area Percent (Abs. Yield g, Mole % Yield)					Identification
1. Neutral Materials	Hydrocarbon Fraction I	II	III	IV	V	
1.00	0.26	trace	trace	0.33		p-$PhC_6H_4CH(Ph)_2$
1.18	0.52	0.56	0.43	0.66		1-p-Cyclohexylphenyl-1,1-diphenylbutane
1.47	50.4	23.8	24.2	22.6	76.1 (0.098, 10.6)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.68	trace	1.19	1.54	1.79		1-p-(1,4-Dihydrophenyl)-phenyl-1,1-diphenylbutane
2.06	45.6	70.4	69.8	70.1	18.6 (0.024, 2.59)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
3.12	3.24	4.0	4.06	4.51	5.35	unknown
VPC conditions: Column (A) temperature, 265°; flow rate, 16 mm; pressure, 40 psig						
2. Acidic Materials as Methyl Esters						
0.50	0.35					unknown
0.65	1.05					"
0.72	0.89					"
1.00	91.1 (0.548, 52.9)					p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.19	2.1					unknown
1.61	4.56					unknown
VPC conditions: Column (A) temperature, 258°; flow rate, 15 mm; pressure, 40 psig						

90 minutes. After cooling down to room temperature, the solution was kept standing for one hour before it was cooled to -75°. In the other flask, 1.54 g (0.223 g-atom) of lithium and 0.1 ml (0.0016 mole) of methyl iodide were placed in 250 ml of distilled THF and the solution was stirred for 10 minutes at room temperature prior to cooling to -75°. A solution of n-butyl chloride (0.943 g, 0.0102 mole) in 10 ml of distilled THF was added to the solution over a period of 20 minutes and followed immediately by the addition of a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.004 g, 0.00253 mole) in 15 ml of distilled THF over a period of 20 minutes. The reaction mixture developed the same color as that of the previous run and was then continuously stirred at -75° for 90 minutes. As soon as the solution developed a black pink color, the stirring was stopped and a 5 ml aliquot was hydrolyzed with methanol (Hydrocarbon VI). To the rest of the reaction mixture was added ca. 150 ml of the potassium t-butoxide solution (freed from potassium metal) in the same manner given in the previous run and the resulting mixture, after a few seconds of slow stirring, was kept standing for 10 minutes at -75°. A 5 ml aliquot was then hydrolyzed with methanol (Hydrocarbon VII) and the remainder was siphoned onto crushed solid carbon dioxide (excess lithium was removed by filtration during carbonation). The carbonated mixtures were worked up as stated in the previous run to give 0.337 g of crude neutral material (Hydrocarbon VIII) and

0.67 g of acid. Gas chromatographic analysis of the Hydrocarbon VI gave a 52.6 to 47.4 ratio of unrearranged (RH) to rearranged hydrocarbon (R'H). On the other hand VPC analysis of Hydrocarbon VII which was hydrolyzed after the addition of the potassium t-butoxide revealed a 24.1 to 75.9 ratio of the former (RH) to the latter (R'H). Quantitative gas chromatographic analyses of Hydrocarbon VIII and acid are noted in Table 24.

In run 3, lithium (1.55 g, 0.244 g-atom) in 250 ml of freshly distilled tetrahydrofuran was activated by addition of 0.1 ml (0.0016 mole) of methyl iodide under the vigorous stirring for 10 minutes at room temperature. After cooling down to -75°, the solution was dried as usual by addition of a solution of n-butyl chloride (0.936 g, 0.0102 mole) in 20 ml of distilled THF over a period of 30 minutes with vigorous stirring. To the mixture was added a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1.011 g, 0.00255 mole) in 25 ml of distilled THF over a period of 25 minutes and then the solution was kept stirring at -75° for an additional 90 minutes until the solution developed a black pink. During this reaction the color change was almost the same to that of the previous runs. A 10 ml aliquot was hydrolyzed with methanol (Hydrocarbon IX) and to the remainder was added rapidly about 6 g (0.05 mole) of commercial potassium t-butoxide* in 50 ml of distilled THF with occa-

*See page 129

Table 24. Gas Chromatographic Analyses of Products from Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Potassium t-Butoxide in THF at -75° (Run 2)

Relative Retention Time	Peak Area Percent (Abs. yield g, Mole % Yield)			Identification
1. Neutral Materials	Hydrocarbon Fraction VI	VII	VIII	
1.00	51.7	23.8	60.1 (0.13, 14.2)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.38	46.5	74.8	32.9 (0.071, 7.77)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
2.12	1.8	1.4	6.97	unknown
VPC conditions: Column (A) temperature, 266°; flow rate, 15 mm; pressure, 40 psig				
2. Acidic Materials as Methyl Esters				
0.65	2.87			unknown
0.72	1.63			"
1.00	89.0 (0.606, 58.4)			p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.19	4.38			unknown
1.62	2.12			"
VPC conditions: Column (A) temperature, 258°; flow rate, 15 mm; pressure, 40 psig				

sional slow stirring. After standing for 10 minutes at the same temperature, a portion of 10 ml aliquot was protonated with methanol (Hydrocarbon X) and the rest of the reaction mixture was carbonated as usual. The usual work-up on the carbonated mixture yielded 0.56 g of neutral material (Hydrocarbon XI) and 0.28 g of acid. Gas chromatographic analyses of the both Hydrocarbon IX and X showed 53 to 47 and 38 to 62 ratios of unrearranged (RH) to rearraned hydrocarbon (R'H) respectively (see Table 25). Quantitative VPC analyses of the Hydrocarbon XI and acid (unrearranged acid was not detected) are also summarized in Table 25.

In run 4, potassium t-butoxide prepared from reaction of 9.56 g (0.244 g-atom) of potassium with 8.78 g (0.0784 mole) of t-butyl alcohol in 300 ml of freshly distilled tetrahydrofuran was kept at room temperature for two hours until one half portion of the solution was siphoned into the organolithium compounds in the other flask. For the latter lithium (0.976 g, 0.141 g-atom) in 250 ml of distilled THF was activated by addition of 0.03 ml of methyl iodide under the vigorous stirring for 10 minutes at room temperature. After cooling down to -75°, n-butyllithium (0.5 ml,

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*In a glove box filled with nitrogen, about 6 g of commercial potassium t-butoxide was weighed to dissolve in THF. After the solution was transferred to a dropping funnel, about 0.2 ml (0.0026 mole, from Gilman titration) of n-butyl lithium was added and the funnel was stoppered in the box until it was attached to the reaction flask.

Table 25. Gas Chromatographic Analyses of Products from Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Commercial Potassium t-Butoxide in THF at -75° (Run 3)

Relative Retention Time	Peak Area Percent (Abs. yield g, mole % Yield)			Identification
1. Neutral Materials	Hydrocarbon Fraction IX	X	XI	
1.00	0.73	0.51	0.3	p-$PhC_6H_4CH(Ph)_2$
1.21	0.28	0.41	0.4	1-p-Cyclohexylphenyl-1,1-diphenylbutane
1.47	50.0	35.7	50.3 (0.214, 23.1)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.06	44.5	58.2	43.6 (0.185, 20.1)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
3.21	4.44	5.14	5.4	unknown
VPC conditions: Column (A) temperature, 267°; flow rate, 15 mm; pressure, 40 psig				
2. Acidic Materials as Methyl Esters				
0.46	1.36			unknown
0.50	4.54			"
0.64	2.38			"
1.00	82.6 (0.212, 20.4)			p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
1.22	1.93			unknown
1.41	7.15			"
VPC conditions: Column (A) temperature, 259°; flow rate, 15 mm; pressure, 40 psig				

0.0065 mole) in pentane was introduced over a period of 10 minutes and then a few drops of a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (3.004 g, 0.00758 mole) in 30 ml of distilled THF was added to the solution under the continuous stirring. Since the reaction had not initiated after 10 minutes, 0.44 g (0.0048 mole) of n-butyl chloride was added to the mixture with stirring for 10 minutes. To the solution was added the rest of the chloride dropwise over a period of 30 minutes and the resulting mixture which had a dark pink color was continuously stirred at -75° for one hour and 30 minutes. A 10 ml aliquot was hydrolyzed with methanol (Hydrocarbon XII) and to the rest of the organolithium solution was added ca. 150 ml of the potassium t-butoxide solution (free of potassium metal) without stirring. After one-half minute of vigorous stirring the mixture was kept standing for 5 minutes until a 10 ml aliquot was protonated with methanol (Hydrocarbon XIII) and the remainder was forced onto the crushed solid carbon dioxide. The usual work-up on the carbonated mixture gave 1.35 g of neutral material (Hydrocarbon XIV) and 1.58 g of acid. According to gas chromatographic analyses, hydrocarbon XII showed a 63 to 37 ratio of unrearranged (RH) to rearraned hydrocarbon (R'H) while Hydrocarbon XIII gave a 31 to 69 ratio of the former (RH) to the latter (R'H). Quantitative VPC analysis of Hydrocarbon XIV and the acid fraction (unrearranged acid was not found) are noted in Table 26. The nmr spectrum of a

Table 26. Gas-Chromatographic Analyses of Products from Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Potassium t-Butoxide in THF (Run 4)

Relative Retention Time	Peak Area Percent (Abs. yield g, mole % yield)				Identification
1. Neutral Materials	XII	Hydrocarbon Fraction XIII	XIV		
1.00	0.83	0.89	trace		p-$PhC_6H_4CH(Ph)_2$
1.14	0.28	0.3	trace		1-p-Cyclohexylphenyl-1,1-diphenylbutane
1.42	61.1	28.5	63.7	(0.644, 23.5)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
1.64		0.99	1.92	(0.019, 0.7)	1-p-(1,4-Dihydrophenyl)phenyl-1,1-diphenylbutane
1.97	35.7	63.2	19.1	(0.194, 7.07)	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
3.0	2.19	6.17	15.3		unknown
VPC conditions: Column (A) temperature, 268°; flow rate, 13 mm; pressure, 40 psig					
2. Acidic Materials as Methyl Esters					
0.45	0.6				unknown
0.49	3.8				"
1.00	95.6	(1.51, 48.8)			p-$PhC_6H_4(CH_2)_3C(Ph)_2CO_2H$
VPC conditions: Column (A) temperature, 255°; flow rate, 13 mm; pressure, 40 psig					

small portion of the acid in CCl_4 was essentially the same as that of the authentic 5-p-biphenylyl-2,2-diphenylpentaoic acid (see page 38), nmr CCl_4), δ 7.25 (19.00 H, m), 2.50 (4.2 H, m), 1.45 (2.1 H, m).

In run 5, to the organolithium compounds (except for a 10 ml aliquot which was hydrolyzed with methanol, Hydrocarbon XV) prepared from the reaction of 1.56 (0.224 g-atom) of lithium with 0.986 g (0.0107 mole) of n-butyl chloride and 0.977 g (0.00246 mole) of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane in 300 ml of THF at -75° for two hours, were added 150 ml of potassium t-butoxide solution (freed from potassium) prepared from 7.72 g (0.197 g-atom) of potassium and 8.9 g (0.12 mole) of t-butyl alcohol in 300 ml of THF. The resulting mixture, after stirring for 3 minutes, was kept standing for 10 minutes at -75° and siphoned into excess methanol (Hydrocarbon XVI). The usual work-up yielded 0.94 g of viscous oily material. Gas chromatographic analysis of the Hydrocarbon XV gave 53.2 to 46.8 ratio of unrearranged (RH) to rearranged hydrocarbon (R'H) while the ratio of the former (RH) to the latter (R'H) in the analysis of the Hydrocarbon XVI was 33.7 to 66.3 (see Table 27). The nmr spectrum of the Hydrocarbon XVI in CCl_4 gave the following spectral data: a multiplet centered at δ 7.1 (19.00 H, aromatic hydrogens); a triplet centered at δ 3.84 (0.6 H, J = 7.5 Hz, a unique hydrogen of the rearranged hydrocarbon); another triplet centered at δ 2.59 (2.1 H, J = 7.5 Hz);

Table 27. Gas Chromatographic Analyses of Products from Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Potassium t-Butoxide in THF at -75° (Run 5)

Relative Retention Time	Peak Area Percent (Abs. yield g, mole % Yield)		Identification
	Hydrocarbon Fraction XV	XVI	
1.00	4.18	1.21	p-$PhC_6H_4CH(Ph)_2$
1.14	0.98	1.74	1-p-cyclohexylphenyl-1,1-diphenylbutane
1.47	49.45 (0.018, 2.3)	32.1 (0.216, 24.2)	p-$PhC_6H_4C(Ph)_2(CH_2)_3H$
2.06	43.5 (0.016, 1.8)	63.2 (0.426, 47.9	p-$PhC_6H_4(CH_2)_3CH(Ph)_2$
3.19	1.89	1.74	unknown

VPC conditions: Column (A) temperature, 265°; flow rate, 15 mm; pressure, 40 psig

broad complex multiplets in the region of δ 1.0 - 2.4, various types of methylene hydrogens; a ca. triplet centered at δ 0.92, ending methyl hydrogens of the unrearranged hydrocarbon. The content of 4-p-biphenylyl-1,1-diphenylbutane in the Hydrocarbon XVI could be roughly estimated as 60 percent from the nmr spectrum.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cs-K-Na Alloy in THF and Measurement of NMR Spectrum of the Resulting Carbanion

In a small glass vial (previously flame dried) containing a glass coated stirrer inside a glove box filled with nitrogen, placed 0.5 ml (0.01 g-atom) of Cs-K-Na alloy* and two ml of freshly distilled tetrahydofuran. Into the solution was dumped 0.192 g (0.000485 mole) of crystalline 4-chloro-1-p-biphenylyl-1,1-diphenylbutane without stirring and the vial was tightly stoppered with a rubber septum. Upon addition of the chloride, a red color appeared instantly on the surface of the alloy. After cooling down to -75°, the solution was stirred for 10 minutes. Upon stirring, the color of the solution changed to a deep red and finally turned black. To the solution was added by means of hypo-

*The alloy was prepared from 10.9 g (0.082 g-atom) of cesium, 3.74 g (0.096 g-atom) of potassium and 0.558 g (0.0243 g-atom) of sodium in 50 ml of dry isooctane at 70° with stirring under an atmosphere of nitrogen.

dermic needle about 3 ml of pure mercury over a period of 20 minutes under a nitrogen atmosphere with the continuous stirring while the color of the reaction mixture slowly turned deep red. After standing for 20 minutes at room temperature a portion of the solution was transferred to a dry nmr tube flushed out with nitrogen and the tube was tightly sealed. Another portion of the mixture was hydrolyzed with ethanol. Gas chromatographic analysis of the ethanolysate at 266° with a flow rate of 13 mm gave the following products in the % yields recorded (calculation based on relative peak areas) 2.73 of an unknown, 1.72 of p-biphenylyldiphenylmethane, 8.19 of 1-p-biphenylyl-1,1-diphenylbutane and 87.4 of 4-p-biphenyl-1,1-diphenylbutane with relative retention times as 0.62, 1.00, 1.46 and 2.08 respectively. The nmr spectrum, measured one hour later (see Fig. 1) gave the following spectral data: a multiplet at δ 7.17 (11.7 H), biphenylyl and non-carbanionic aromatic hydrogens; another multiplet at δ 6.87 (7.8 H, the highest peak), ortho and meta phenyl hydrogens in carbanion; a triplet centered at δ 5.84 (2.00 H, J = 6.7 cps), para phenyl hydrogens in carbanion; another triplet centered at δ 3.65, α-methylene hydrogens of solvent THF; a quintet centered at δ 1.78, β-methylene hydrogens of solvent THF. The multiplet peak at δ 6.87 actually consisted of four unsymmetrical peaks at δ 7.03 overlapped with the peak of the biphenylyl and non-carbanionic aromatic hydrogens at δ 6.87, 6.70 and 6.54. The delta values of the spectrum were

calculated relative to the value of the α -methylene hydrogens of the solvent THF as δ 3.65. (The nmr spectrum of THF gave a triplet at δ 3.65 and a quintet at δ 1.78 with internal tetramethylsilane as standard). According to the nmr spectrum the content of carbanion in the reaction product was estimated to be 87 percent. But 24 hours later the content of the carbanion in the product decreased to 54 percent according to the nmr spectrum in which the relative intentsities were 17.5:8.2:2.0 for the ratio of biphenylyl and non-carbanionic aromatic hydrogens: ortho and meta hydrogens in carbanion; para hydrogens in carbanion, respectively. The carbanion in the sealed nmr tube seems quite stable since the carbanion solution still showed intense red color even after a month standing the refrigerator.

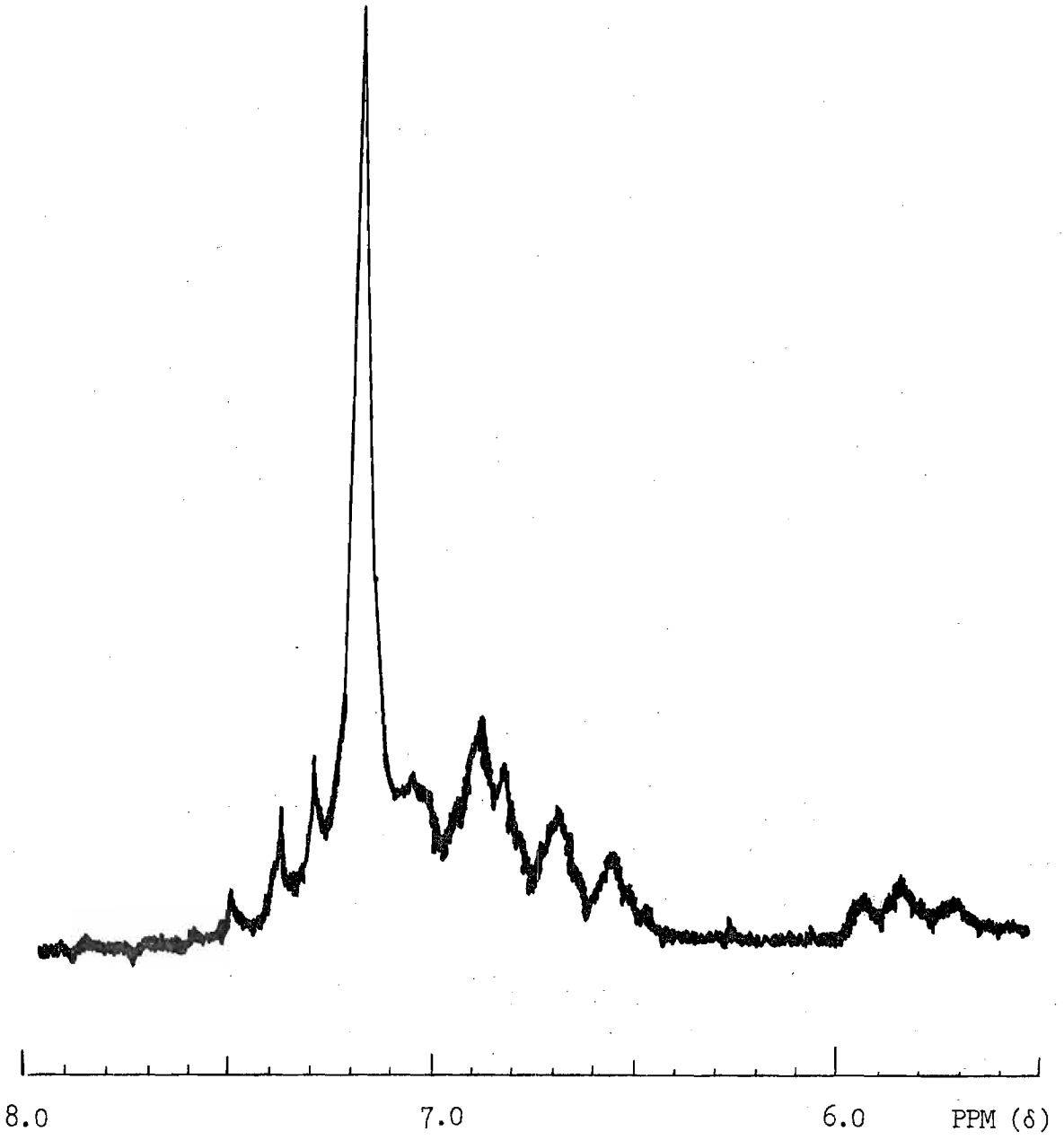


Figure 1. NMR Spectrum of 4-p-Biphenylyl-1, 1-diphenyl-butyl Anion.

CHAPTER V

DISCUSSION

Synthesis

4-Chloro-1-p-biphenylyl-1,1-diphenylbutane and 1-p-biphenylyl-1,1-diphenylbutane

The chloride was prepared in overall yield of about 12 percent from the synthetic route shown below. The first intermediate p-biphenylyldiphenylcarbinol was prepared in 42 percent yield from the reaction[29] of p-bromobiphenyl with lithium and subsequent addition of benzophenone in dry ether solution. A 95 percent yield of the second intermediate p-biphenylyldiphenylchloromethane was obtained from the reaction[31] of pure p-biphenylyldiphenylcarbinol with acetyl chloride (but the average yield was about 73 percent in other reactions).

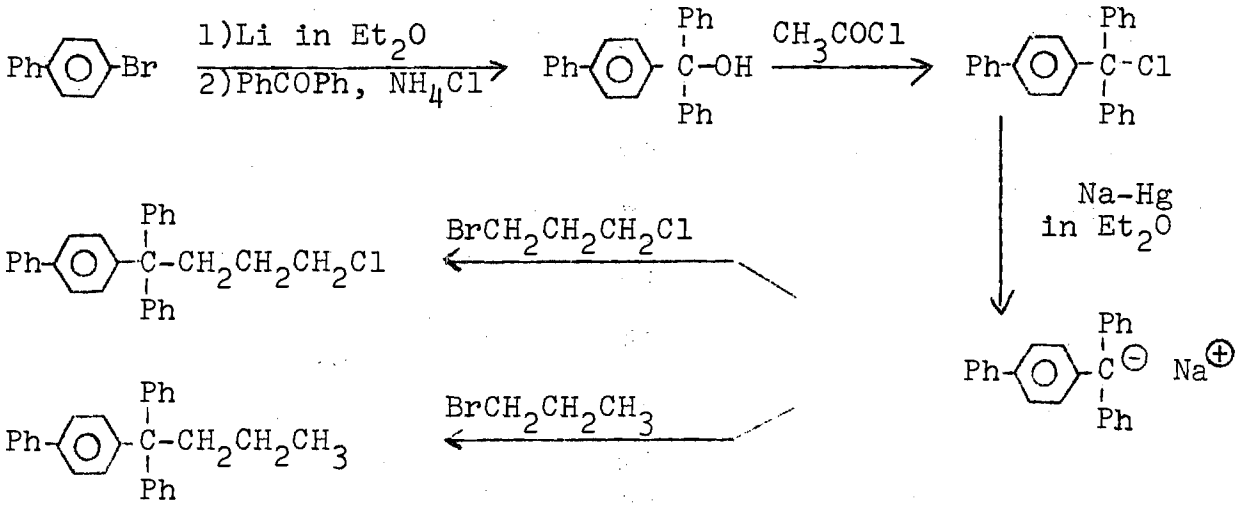


Figure 2. Synthetic Route to 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane and 1-p-Biphenylyl-1,1-diphenylbutane.

Since difficulty was encountered in purification of the chloride from the reaction of p-biphenylyldiphenylmethylsodium with 1-bromo-3-chlorpropane, the yield of the chloride in this step was only about 37 percent. The hydrocarbon, 1-p-biphenylyl-1,1-diphenylbutane was prepared by reacting the p-biphenylyl-diphenylmethylsodium with 1-bromopropane.

5-p-Biphenylyl-5,5-diphenylpentanoic acid

This acid was prepared by the synthetic route shown below. The reaction of 4-chloro-1-p-biphenylyl-1,1-diphenyl-butane with sodium cyanide in presence of sodium iodide in dimethyl sulfoxide at room temperature gave about 96 percent yield of 5-p-biphenylyl-5,5-diphenylpentanenitrile according to the general procedure of Cope and Metha.[37] Since attempted recrystalization of the nitrile from various solvents was not successful, the nitrile was hydrolyzed with potassium hydroxide in ethylene glycol without prior purification according to the general procedure given in "Organic Syntheses".[38] The acid was obtained in 95 percent yield from the nitrile.

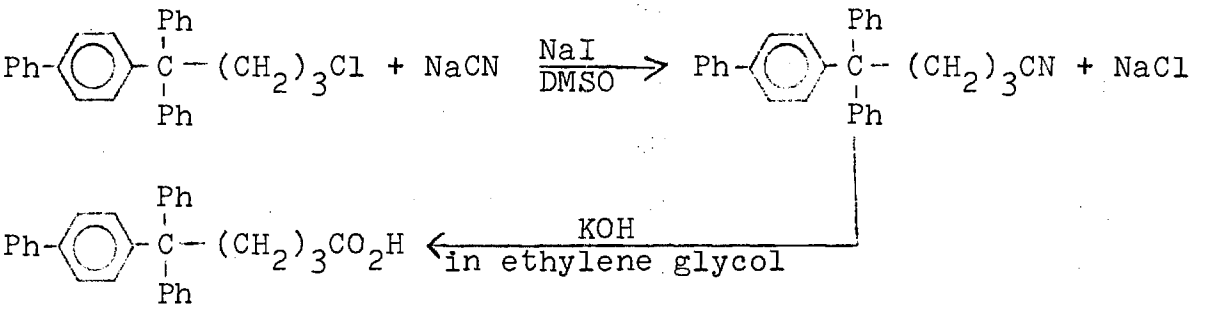


Figure 3. Synthetic Route to 5-p-Biphenylyl-5,5-diphenyl-pentanoic Acid.

5-p-Biphenylyl-2,2-diphenylpentanoic Acid and 4-p-Biphenylyl-1,1-diphenylbutane

The preparation[7] of the title acid and hydrocarbon followed the synthetic route shown below. The first intermediate 4-p-biphenylyl-1,1-diphenylbutanol-1 was prepared in 79 percent yield from reaction of phenylmagnesium bromide with methyl 4-p-biphenylylbutanoate according to the general procedure given in "Organic Syntheses".[39] The converstion of this carbinol to the corresponding methyl ether was carried out in 92 percent yield by reacting the carbinol with absolute methanol in presence of sulfuric acid according to the general procedure of Ziegler and coworkers.[40] The reaction of the 1-methoxy-4-p-biphenylyl-1,1-diphenylbutane with molten potassium in THF at reflux with high-speed stirring and subsequent carbonation of two thirds of the deep red reaction mixture gave the desired acid, 5-p-biphenylyl-2,2-diphenylpentanoic acid.

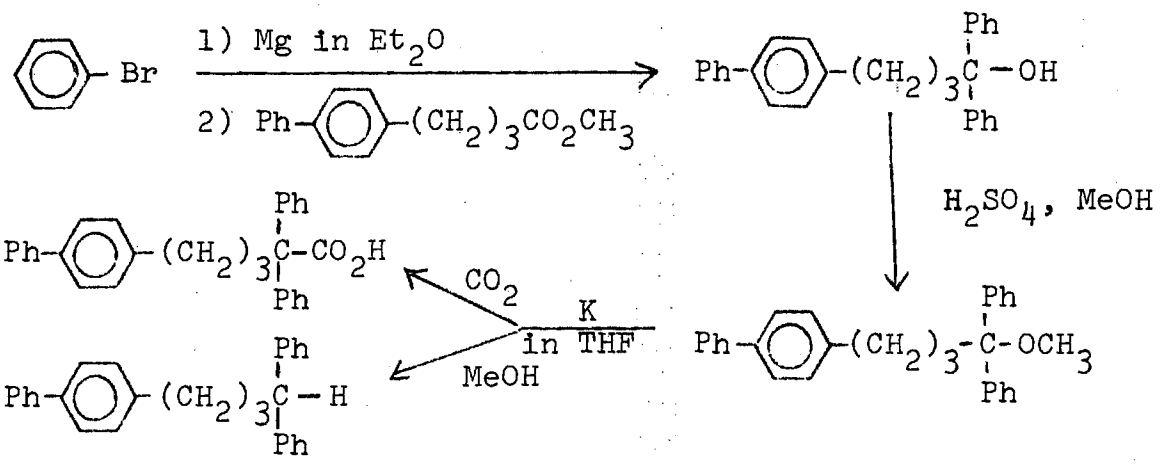


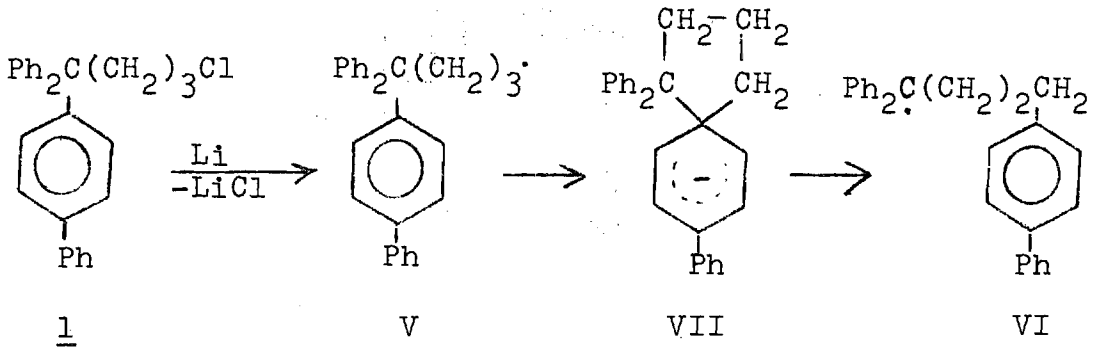
Figure 4. Synthetic Route to 5-p-Biphenylyl-2,2-diphenylpentanoic Acid and 4-p-Biphenylyl-1,1-diphenylbutane.

Protonation of the remainder of the reaction mixture with methanol gave the hydrocarbon, 4-p-biphenylyl-1,1-diphenylbutane.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Metal in THF at -70°

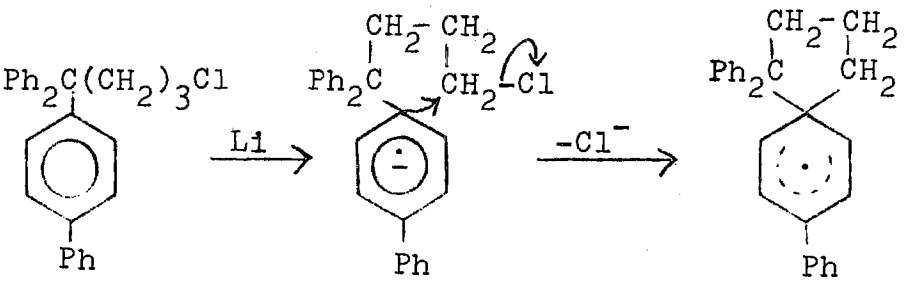
Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with lithium in THF at -70° gave an organolithium reagent, of which an aliquot was hydrolyzed. Analysis by gas chromatography showed the presence of a 76 to 24 ratio of 1-p-biphenylyl-1,1-diphenylbutane (2) to 4-p-biphenylyl-1,1-diphenylbutane (3). The bulk of the solution was filtered (to remove excess lithium) and allowed to stand for 4 hours at 0°. Hydrolysis of an aliquot now showed a 69 to 31 ratio of 1-p-biphenylyl-1,1-diphenylbutane (2) to 4-p-biphenylyl-1,1-diphenylbutane (3). Carbonation of the remainder gave 3.6 parts of hydrocarbons to 1 part of carboxylic acids; the hydrocarbons consisted of an 81 to 19 ratio of 1-p-biphenylyl-1,1-diphenylbutane (2) to 4-p-biphenylyl-1,1-diphenylbutane (3), while the acids contained a 17 to 83 ratio of 5-p-biphenylyl-5,5-diphenylpentanoic acid to 5-p-biphenylyl-2,2-diphenylpentanoic acid. Surprisingly most of the rearrangement took place during reaction of the chloride (1) with lithium metal at -70°; very little additional rearrangement (only ca, 7%) took place during storage at 0. As expected upon storage at 0, 4-p-biphenylyl-4,4-diphenylbutyllithium (I) abstracted a proton from the solvent THF to give

1-p-biphenylyl-1,1-diphenylbutane (2) faster than did the rearranged product 4-p-biphenylyl-1,1-diphenylbutyllithium (II) to give 4-p-biphenylyl-1,1-diphenylbutane (3); the result was that the carboxylic acids were largely of rearranged structure while the hydrocarbons from carbonation were largely of unrearranged structure. It is, therefore, believed that the present result - 24% rearrangement during the low temperature reaction with lithium metal at -70° but little additional rearrangement upon warming the organolithium compound (I) to 0° - imply that the rearrangement at low temperature occurs in a intermediate free radical V which rearranges to the spiro derivative VII;



1 V VII VI

Alternatively, the starting chloride (1) may be first reduced to the corresponding radical anion VIII which is then converted to VII;



1 VIII VII

The converstion of the radical anion VIII to the spiro anion VII could be via radical V but a more attractive path would be for VIII to proceed directly to VII by biphenylyl radical anion participation. The spiro intermediate VII may then ring open to give 4-p-biphenylyl-1,1-diphenylbutyl radical VI which is then reduced by lithium to 4-p-biphenylyl-1,1-diphenyl anion II or, alternatively, the reduction of VII by lithium may precede ring opening.

Rearrangement during the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with lithium appears similar to, but is much more extensive, than that during reaction of 1-chloro-2-methyl-3-phenylpropane (neophyl chloride) with lithium.[9] It is also related to the mechanism which has been proposed to explain the formation of methylcyclopropane during reaction of 5-hexenyl halides with sodium naphthalenide.[15c]

The additional rearrangement (ca. 7%) which took place during storage of the lithium reagent from 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) at 0°. This result suggested to attribute to carbanion rearrangement of 4-p-biphenylyl-4,4-

diphenylbutyllithium (I). While it is possible in principle for a carbanion to exist in mobile equilibrium with the corresponding radical:

$$RCH_2^{-} \rightleftharpoons RCH_2\cdot + e^{-}$$

the absence of any general evidence that simple organolithium compounds such as n-butyllithium form free radicals at 0° prompts us to assert that it is the carbanion (or organolithium compound) itself which is undergoing slow rearrangement. In the present work, reaction of lithium with 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) in THF at -70° gave a 76 to 24% mixture of unrearranged organolithium product but when the ratio of lithium metal to chloride was increased from 15:1 to 65:1 a 53 to 47% mixture of unrearranged to rearranged product was obtained. Since in the experiments which have been discussed, reaction takes place presumably at the surface of the lithium metal, the radical V and VI are thought to exist at or near the surface of the lithium and, therefore, are likely not completely "free" radicals. Such heterogeneous reactions are accordingly hard to understand in detail; in particular, it is difficult to understand why the percentage of rearrangement increases with increasing ratio of lithium to organic halide.*

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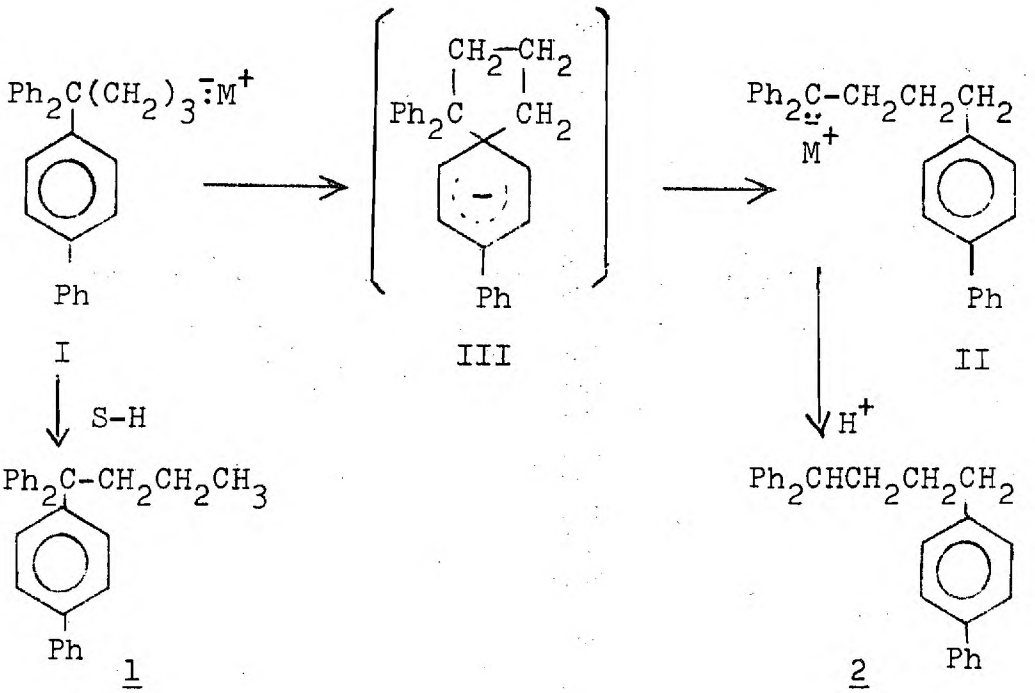
*Various postulates might be entertained such as that rearrangement is induced by impurities in the lithium metal (Lithium Corporation of America, containing 0.5% maxima Na) or by certain (unknown) characteristis of the surface of the lithium.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with the Metals Potassium and Cesium

In contrast to lithium reactions, reaction of the chloride (1) with finely divided potassium metal in boiling THF gave a dark red solution which upon carbonation yielded only 5-p-biphenylyl-2,2-diphenylpentanoic acid (mp. 191-192°) or upon decomposition with methanol gave 4-p-biphenylyl-1,1-diphenylbutane (3), mp. 81-82°, containing only some 1% of 1-p-biphenylyl-1,1-diphenylbutane (2). Reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with cesium over a period of four mintues in boiling THF gave the same rearranged carbanion according to gas chromatographic analyses of the products from carbonation and protonation. These results suggest that both 4-p-biphenylyl-4,4-diphenylbutylcesium and -potassium undergo very readily 1,4 migration of p-biphenylyl.



Alternatively rearrangement could take place in the compounding free radical V as observed with lithium metal.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Potassium Metal in Various Media

In view of the fact that phenyl groups are known to undergo 1,4 migration in free radicals,[41] to establish the reaction mechanism of 1,4 migration of p-biphenylyl in reactions of the chloride (1) with potassium or cesium metal the experiments summarized in Table 28 were performed. In experiments designed to trap the intermediate anion I, the chloride (1) was allowed to react at 65° in THF with increments of potassium and t-butyl alcohol, the latter always in slight excess. Gas chromatographic analysis of the reaction mixture at intervals revealed that 1-p-biphenylyl-1,1-diphenylbutane (2) was an initial product of the reaction; the maximum yield of 1-p-biphenylyl-1,1-diphenylbutane (2) was 18 percent, but this product largely disappeared with continued reduction by excess potassium. The final product consisted of 3 percent of 1-p-biphenylyl-1,1-diphenylbutane (2), 90 percent of 1-p-cyclohexylphenyl-1,1-diphenylbutane (a derivative of the unrearranged hydrocarbon), and 6 percent of an unknown. The unknown compound is evidently a 1,4-dihydro derivative of 1-p-biphenylyl-1,1-diphenylbutane

41. (a) S. Winstein, R. Heck, S. Lapporte, and R. Baird, Experimenta, 12, 138 (1956); (b) W. H. Starnes, J. Amer. Chem. Soc., 85, 3708 (1963); (c) H. Sakuri and A. Hosomi, ibid., 92, 7507 (1970); (d) M. Julia and B. Malassine, Tetrahedron Lett., 987 (1971).

(2) since (unlike 1-p-cyclohexylphenyl-1,1-diphenylbutane which was unaffected) it gave 1-p-biphenylyl-1,1-diphenylbutane (2) upon treatment with 5 percent Pd-C at 100°. The structure of 1-p-cyclohexylphenyl-1,1-diphenylbutane was confirmed by its mass spectrum (peaks at m/e 368 and 325) and nmr spectrum. While the results are somewhat complicated by reduction of the biphenylyl nucleus, this Table shows that, whereas the chloride (i) reacts with potassium in THF with essentially completely 1,4 migration of the p-biphenylyl group, in presence of excess t-butyl alcohol rearrangements is completely blocked. With the less effective proton donor, triethylcarbinol, rearrangement is much more extensive; with the still less acidic n-butylamine, rearrangement is almost as complete as in pure tetrahydrofuran. Since the extent of rearrangement varies inversely with the proton donor ability which is approximately constant in Exp. 1 - 5 of Table 28), the results agree well with the idea that it is a carbanion (or an organoalkali compound) which is undergoing rearrangement and which is trapped prior to rearrangement by addition of weak acids. Put in other words, since alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from t-butyl alcohol,[42] the intermediate trapped

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42. (a) W. A. Pryor and R. W. Henderson, J. Amer. Chem. Soc., 92, 7234 (1970); (b) W. A. Pryor and J. P. Stanley, ibid., 93 (1971); (c) W. A. Pryor, Chem. & Eng. News, June 7, 42 (1971).

Table 28. Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Alkali Metals in Various Media

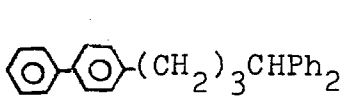
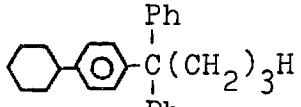
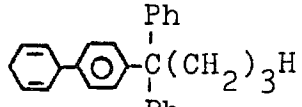
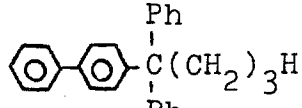
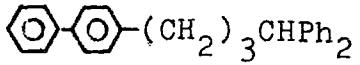
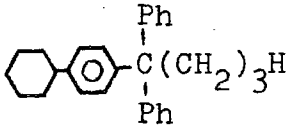
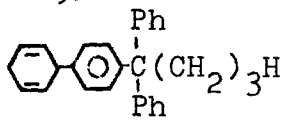
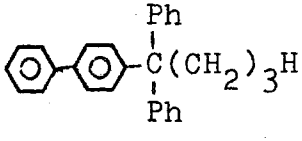
Exp. No.	Conditions	Products, % 			
1.	React with K in THF at 65° and then add CH_3OH	97.6	0	0	1.4[a]
2.	2.6 mmoles RCl with 5.8 mg-at. of K + 13 mmoles t-BuOH in THF at 65°	0	13.8	-	12.5[b]
3.	The reaction mixture from (2) treated several times successively with 6 mg-at. of K and 6 mmoles t-BuOH at 65° in THF	0	90	5.8	3.4
4.	2.3 mmoles RCl with 7.1 mg-at. of K and 6.8 mmoles of $(CH_3CH_2)_3$-COH at 65° in THF	43	7.2	6.7	7.2[c]

Table 28. Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Alkali Metals in Various Media (Continued)

Exp. No.	Conditions	Products, % 			
5.	2.7 mmoles RCl with 5.8 mg-at. of K and 12.5 mmoles of n-$BuNH_2$ at 65° in THF and then addition of CH_3OH	95	0	0	4.5

[a]There was also found 0.8% of $Ph_2CHCH_2CH_2CH_3$ and 0.2% of p-$PhC_6H_4CHPh_2$.

[b]The remainder was unreacted RCl.

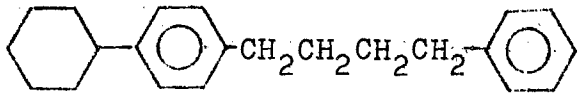
[c]The remainder consisted of 25% of unreacted RCl and 9% of an unknown.

by addition of small amounts of t-butyl alcohol in these experiments must be carbanion I rater than the corresponding free radical V.

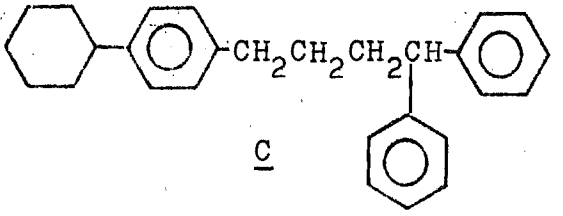
Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Various Alkali Metals in Dioxane.

In these experiments, the effect of changing solvent from tetrahydrofuran to dioxane is investigated. In both tetrahydrofuran and dioxane, potassium reacts with 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) to give almost exclusively products of 1,4 migration of p-biphenylyl; in tetrahydrofuran at 65° the products is the corresponding 4-p-biphenylyl-1,1-diphenylbutyl anion (II) whereas in dioxane it is predominantly the corresponding hydrocarbon. Evidently dioxane at 101° is more acidic (toward carbanions) than tetrahydrofuran at 65° (although tetrahydrofuran is better hydrogen atom donor than dioxane).[42] In contrast to potassium, sodium metal in dioxane gives predominantly the unrearranged hydrocarbon, 1-p-biphenylyl-1,1-diphenylbutane (92%). The inequality in rate between sodium and potassium compounds in carbanion rearrangements has not been previously observed although it has been known for some time that organolithium compounds rearrange more slowly than organosodium or -potassium compounds.[4,5] In a continuation of these studies the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with cesium in dioxane was investigated at 30° to 40°. The product with a deficiency

of cesium was a 4 to 96 ratio of unrearranged to rearranged hydrocarbon (p-$PhC_6H_4CPh_2CH_2CH_2CH_3$ and p-$PhC_6H_4CH_2CH_2CH_2CHPh_2$ respectively). The expected rearranged organocesium product was not found but only its product of protonation. Dioxane is therefore much more acidic than tetrahydrofuran even at 30° to 40°. With use of an excess of cesium metal the yield of volatile products after carbonation is greatly reduced and consisted primarily of the hydrocarbons, 4-p-cyclohexylphenyl-1-phenylbutane (compound A, 11.7% yield) and 4-p-cyclohexylphenyl-1,1-diphenylbutane (compound C, 15.6% yield). The compound C is evidently a reduction product of 4-p-biphenylyl-1,1-diphenylbutane (3) while compound A seems to be a cleavage product of compound A.



A

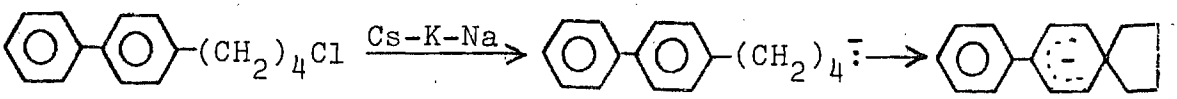


C

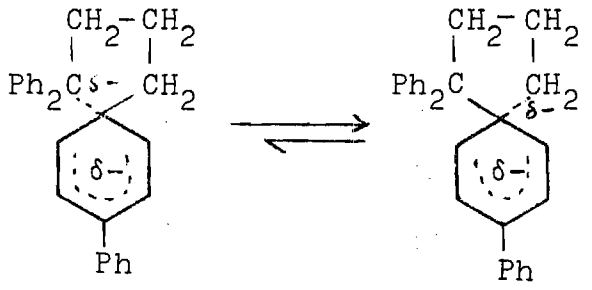
The compound C is rather similar to the major reduction product obtained previously with potassium metal in THF in the presence of t-butyl alcohol. The solvent dioxane, therefore, seems to play the same role as proton donor in these reductions as does t-butyl alcohol in tetrahydrofuran.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Cs-K-Na Alloy; NMR Spectrum of Resultant Carbanion

According to the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with cesium or potassium metal the spiro anion III is an intermediate in the carbanion rearrangement. In an attempt to detect this intermediate the chloride (1) was allowed to react with excess of finely divided Cs-K-Na euthetic[11] in THF at -75° for some three minutes before carbonation. There was obtained, however, only the usual product of rearrangement, 5-p-biphenylyl-2,2-diphenylpentanoic acid. This result implies that the spiro anion III rearranges readily to carbanion II even at -75°. Ready ring opening of this spiro anion III may be dependent upon the presence of the two phenyl groups which stabilize the final anion II. In contrast to this result, reaction[1] of 4-chloro-1-p-biphenylylbutane (in which the activating phenyls have been replaced by hydrogen) with excess of Cs-K-Na alloy at -70° and subsequent carbonation gave an acid which consisted of 96% of 8-phenylspiro[4.5]-deca-6.9-dienyl 8-carboxylic acid and 4% of 2-p-biphenylylpentanoic acid. Moreover, the nmr spectrum (at 40°) of the carbanion solution from treatment of 4-chloro-1-p-biphenylylbutane with Cs-K-Na alloy in THF-d_8 at -70° [(δ 6.9 - 6.7 (5H, m), 6.30 (2H, d, J = 10 Hz), 4.40 (2 H,d, J = 10 Hz), 1.72 (4H, m), 1.43 (4H, m)] showed conclusively that the major intermediate was the spiro anion, 9-phenylspiro[4.5]-deca-6,9-dienyl anion:



It was, therefore, of interest to check the structure of the carbanion in present work by nmr spectroscopy to see whether it is the rearranged carbanion II or the intermediate spiro anion III which gave rise to the ring opening product (rearranged product) by carbonation and protonation. Alternatively it could be a non-classical carbanion IX or in equilibrium between non-classical carbanion IX and X;



IX X

The carbanion solution from the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with Cs-K-Na alloy in THF at -75° and addition of excess mercury to remove excess alkali metal and destroy radical anion gave the following spectral data at 40°: nmr (in THF): δ 7.17 (11.7 H, m, ordinary aromatic hydrogens), 6.87 (7.8 H, m, ortho and meta hydrogens of diphenylmethyl anion group), 5.84 (2.00 H, t, J = 6.7 cps,

para hydrogens of diphenylmethyl anion group). This spectral data is comparable with those[43] of the triphenylmethyllithium [δ 7.31 (2 H, t, ortho hydrogens), 6.52 (2 H, t, meta hydrogens), 5.96 (1 H, d, para hydrogens)] and diphenylmethyllithium [δ 6.52 (4 H, m, ortho and meta hydrogens), 5.65 (1 H, m, para hydrogens)] in THF. By judging from the observed chemical shifts of the aromatic protons, the carbanion in the present work must be the rearranged carbanion II rather than the spiro anion III (which should have an nmr spectrum similar to 8-phenylspiro[4.5]-deca-6,9-dienyl anion), or the non-classical carbanions IX and X. To be sure if the interaction of the diphenylmethyl group in IX with the p-biphenylyl group (see dashed line in structure IX) is small this structure might be indistinguishable from the more conventional structure II.

Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF

In view of the complications which were encountered in the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) with lithium metal, the homogeneous reaction of this halide was run with lithium biphenyl dissolved in THF at -65°. Since radical anions can transfer but one electron upon collision with an alkyl halide, they should give rise to an inter-

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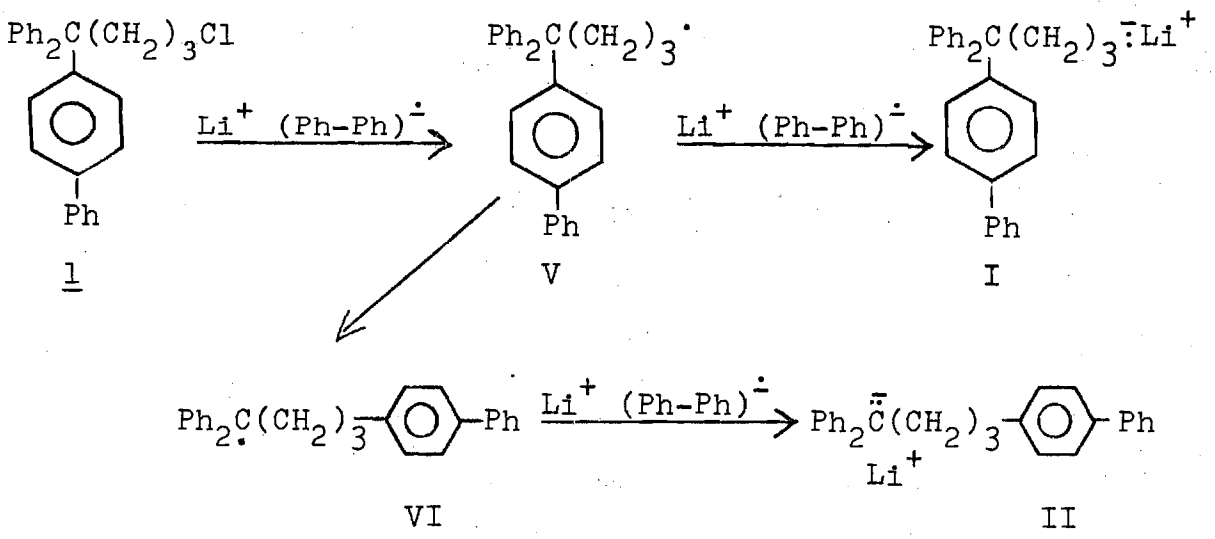
43. V. R. Sandel and H. H. Freedman, J. Amer. Chem. Soc., 85, 2328 (1963).

mediate free radical,[8] radical V in the present work. Again the final outcome must be a competition between rearrangement to radical VI versus reduction to unrearranged organolithium compound I. In the homogeneous case, however, some control over these competitive paths can be obtained by adjusting the concentration of the reducing agent lithium biphenyl.



The results for dropwise addition of a solution of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane (1) to a well stirred solution of > 100% excess lithium biphenyl in THF at -75° followed by decomposition with methanol are that with 0.013 M lithium biphenyl a 12:88 ratio of rearranged to unrearranged hydrocarbon (p-$PhC_6H_4CH_2CH_2CH_2CHPh_2$ and p-$PhC_6H_4CPh_2CH_2CH_2CH_3$, respectively) was produced while with 0.23 M lithium biphenyl a 2:98 ratio of the former to the latter hydrocarbon was obtained. It is notable, therefore, that the amount of rearrange-

ment decreases with increasing concentration of lithium biphenyl. At the higher concentration of lithium biphenyl it is possible to prepare the organolithium product from one gram of the present chloride (1) in absolute yields of 40 to 55 percent (based on the results of carbonation) with only 2 to 3 percent of the organolithium product being of the rearranged structure. A similar technique applied to neophyl chloride [$Ph_2C(CH_3)_2CH_2Cl$] gave the expected organolithium compound with no more than 1.2 percent rearrangement as contrast to 6.4 percent rearrangement[9] during direct reaction of this chloride with lithium metal).

Reaction of 4-p-Biphenylyl-4,4-diphenylbutyllithium with Potassium t-Butoxide in THF

Having discovered how to make 4-p-biphenylyl-4,4-diphenylbutyllithium (I) with an only negligible amount of its rearrangement product 4-p-biphenylyl-1,1-diphenylbutyllithium (II), efforts were directed toward how to make I rearrange to II. It has already been noted that 4-p-biphenylyl-4,4-diphenylbutyllithium (I) rearranges to 4-p-biphenylyl-1,1-diphenylbutyllithium (II) only very slowly even at 0° such that attempts to produce the rearrangement product by warming a solution of 4-p-biphenylyl-4,4-diphenylbutyllithium (II) result primarily in unrearranged hydrocarbon by proton abstraction from the solvent tetrahydrofuran. Accordingly a catalyst has been looked for to promote this rearrangement

in the cold (-75°). Since potassium t-butoxide has been found to activate butyllithium toward metallation of hydrocarbons such as toluene[21] and benzene,[44] its efficacy in promoting rearrangement of the organolithium compound I has now been tested. Addition of excess potassium t-butoxide to a solution of 4-p-biphenylyl-4,4-diphenylbutyllithium (I) at -75° resulted within 10 minutes (or less) in complete disappearance of I and appearance of rearranged organoalkali compound of the carbon skeleton of II as shown by products of carbonation and protonation.

This process of catalysis of the rearrangement of an organolithium compound by potassium t-butoxide (a Lewis base) is somewhat analogous to the catalysis of the Wagner-Meerwein rearrangement of an alkyl halide by aluminum chloride (a Lewis acid). In the former case the potassium t-butoxide gives rise to a more or less "free" carbanion, while in the latter case aluminum chloride gives a more or less "free" carbonium ion; both ions then rearrange. It is believed that the demonstration of potassium t-butoxide catalysis of the rearrangement of 4-p-biphenylyl-4,4-diphenylbutyllithium (I) helps to settle the question of the mechanism of such rearrangement, i.e., it is logical to suppose that such a strong base could catalyze an anionic rearrangement, but unlikely that such a catalyst would initiate free-radical or carbonium ion processes.

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44. M. Schlosser, J. Organometal. Chem., 8, 9 (1967).

The details of the present catalysis is uncertain but the simplest explanation is that the corresponding organopotassium compound is formed, i.e.,

$$RLi + KO\underline{t}\text{-}Bu \longrightarrow R\bar{:}K^{+} + LiO\underline{t}\text{-}Bu$$

Since organopotassium compounds[22] may be precipitated from hydrocarbon solution by reaction of organolithium compounds with potassium alkoxides. In other cases, however, complex aggregates[21] of the type $RLi\cdot(KO\underline{t}\text{-}Bu)_x$ or $RLi\cdot(RK)_x$ may be precipitated. One peculiarity of the present work on potassium t-butoxide catalysis is that the product, after decomposition with methanol, shows a ratio of unrearranged to rearranged hydrocarbon of about 25 to 75 whereas with potassium metal on the same halide in boiling tetrahydrofuran the ratio is 4 to 96 (after correction for Birch reduction of initial products). These results suggest that potassium t-butoxide catalyzes not only the rearrangement of the organolithium compound but also its protonation by solvent prior to rearrangement. Put in other words, the species were undergoing rearrangement does not appear to be simply the organopotassium compound since the ratio of unrearranged to rearranged hydrocarbon is too high. Additional work, however, is needed to confirm this interpretation since species proton donors may have been present in the reactions catalyzed by potassium t-butoxide (e.g., t-butyl alcohol).

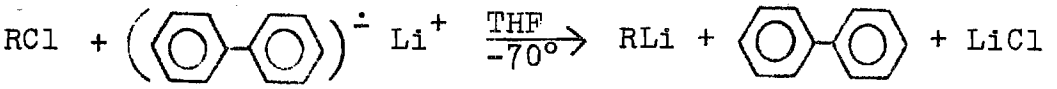
CHAPTER VI

RECOMMENDATIONS

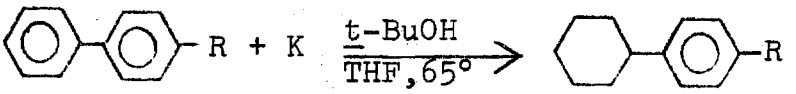
It would be of interest to extend the study of the catalyzed rearrangement observed from the reaction of 4-p-biphenyl-yl-4,4-diphenylbutyllithium with excess potassium t-butoxide to other related organolithium compounds. For this purpose, 4,4,4-triphenylbutyllithium would be an ideal compound to test for 1,4 phenyl migration since it failed to undergo 1,4 phenyl migration in THF at low temperature even though its corresponding potassium compound underwent ortho-cyclization in THF at reflux temperature.[11] Furthermore, since the reaction mechanism of the catalytic rearrangement of the organolithium compound has not been studied, it would be interesting to study the reaction in kinetic detail. Will a trace of potassium t-butoxide induce rearrangement or is a full stoichiometric amount required?

Study of the catalytic rearrangement of organolithium compounds with cesium t-butoxide would also be an interesting subject for comparison with the present work with potassium t-butoxide.

The possibility of using lithium biphenyl in THF for synthesis of organolithium compounds from alkyl halides would be an interesting topic for study.



Synthetic applications of the reaction of p-alkylbiphenyls with potassium metal in THF at reflux in presence of t-butyl alcohol (or some other alcohols) for preparation of pcyclohexylalkylbenzenes is also an interesting subject for study.



APPENDIX I

NMR Spectrum of Acids from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 5)

As shown in Chapter IV (page 111), the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane with excess lithium biphenyl in THF at -75° and subsequent carbonation gave an acid which according to VPC analysis of the methyl ester consisted of 30.1% of unknown Compound E, 2.43% of 5-p-biphenylyl-2,2-diphenylpentanoic acid, 59.7% of 5-p-biphenylyl-5,5-diphenylpentanoic acid (F), and 7.7% of several unknowns. Since unknown Compound E was a significant component of this mixture, the nmr spectrum of the mixture was checked in carbon tetrachloride as solvent (see Table 29). According to the spectrum which showed several characteristic signals such as those of vinyl, allylic and methyl hydrogens, Compound E appeared to be the acid of Birch reduction, 4'-(1",1"-diphenylbutyl)-1,4-dihydrobiphenyl-4-carboxylic acid. In Table 29, the calculated absorption for a 1 to 2 mixture of E with 5-p-biphenylyl-5,5-diphenylpentanoic acid (F) agreed well with the observed absorption. This compound E is thought to be produced by further reduction of one of the abundant products, 1-biphenylyl-1,1-diphenylbutane, with excess lithium biphenyl since biphenyl groups are subjected

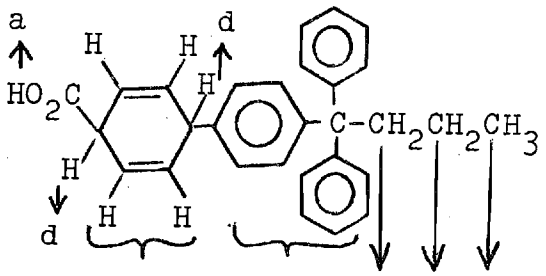
to easy reduction. In Table 29, the intensity of aromatic hydrogen (b) showed some deviation from that of the calculation. This could be explained if this acid mixture contains some of the Birch reduction product 1,4-dihydrobiphenyl-4-carboxylic acid (very short vpc retention time) since excess biphenyl might be competing with 1-p-biphenylyl-1,1-diphenylbutane during the reaction to give the acid, 1,4-dihydrobiphenyl-4-carboxylic acid.

Table 29. NMR Spectrum of Mixture of Acids from Reaction of 4-Chloro-1-p-biphenylyl-1,1-diphenylbutane with Lithium Biphenyl in THF at -75° (Run 5)

δ Value	Multiplicity	Observed Intensity	Calculated Intensity*	Assignment**
11.6	s	1.00	1.00	carboxylic (a)
7.22	m	13.9	17.2	aromatic (b)
5.97	q	1.4	1.33	vinyl (c)
3.72	m	0.67	0.67	allylic (d)
2.62	m			methylene (e)
2.28	(overlapped)	3.3	3.3	methylene (f)
1.27	m (overlapped)	2.3	2.0	methylene (g)
0.90	t	1.0	1.0	methylene (h)

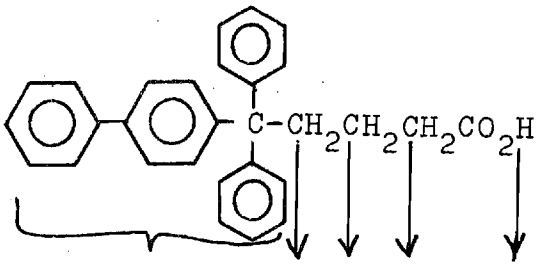
*Calculated for a 1 to 2 mixture of E and F.

**



c b f g h

E



b f g e a

F

APPENDIX II

MASS SPECTRA OF COMPOUND A, B, C, & D

1. Compound A(4-p-Cyclohexylphenyl-1-phenylbutane)

Molecular Formula: $C_{22}H_{28}$

Exact Mass: Calcd., 292.2191;[1] obs., 292.2204[2]

m/e	Rel Abund[3]	Rel. Abund[4]	Struct[5]	m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]
294	1.5	3.2		181	1.5		
293	9.2	18.8		175	1.8	1.5	
292	38	70.5	a	174	6.2	8.8	
291	1.3	1.5		173	31.2	49	f
290	2.2	3		172	1.2	1	
250	1.4	2.8		171	5.3	4	g
249	4.8	8.8		167	3		
248		1.4		165	1		
237	2.2	2.5		161	0.8	1.5	
236	6.7	8.8		160	8	5	
224	1.3	1.8		159	40	29.5	h
223	3	5		158	2.5	1.5	
211	1.8	2		157	3	2.7	
210	17.7	5	b	152	1		
209	1	1		146	1		
208	1.2	1.2		145	2.5		
207	1.7	2		143	2.7		
202	0.6	1		142	1.5		
201	3	4	c	141	2		
193	1			134	1		
187	1	1	d	133	5.5	6	i
186	1	1.5	e	132	7.3	6.8	

1. Compound A (Continued)

m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]	m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]
131	56	44	j	80	1.2	1	
130	6	10		79	4.6	4.2	u
129	8.8	15	k	78	2.8	2.6	
128	4.3	8.8		77	5.5	5.8	v
127	1.5	2.5		76	1		
120	1.2			71	0.6	3. 5	
119	6	4.8	l	70	0.5	1.5	
118	11.2	12	m	69	2	5.5	
117	41	47	n	68	0.6	1	
116	7.2	5.3		67	4.3	3.2	
115	11.5	13.8	o	66	1.4		
112	1			65	5.2	4	
106	2.8	3		63	1.5	1.2	
105	14.2	14	p	60	1		
104	10.5	18.5	q	58	0.5	4.2	
103	3.6	5.5		57	1.5	3.5	
102	1.3	1.8		56	1	1.5	
97		2.8		55	12.7	7.5	w
96	0.5	1		53	3	1.5	
	1.5	2.5		51	3	2	
94	0.6	1		50	1		
93	3	3		44	1.2	3	
92	19	19		43	2	9	x
91	100.0	100.0	r	42	1	1.5	
90	0.5	1.4		41	1.3	3.8	y
89	1.5	2		40	3	1.5	
85		2.2		39	5.8	1.7	
84	1	1.6		32	6.5	3.8	
83	9	11	s	29	3.7	1.5	
82	3.7	2.5		28	23	20.7	z
81	8.6	6	t	27	3.5	1.5	

1. Compound A (Continued)

[1]Atomic Weights:[45] C^{12}, 12.000000; H^{1}, 1.007825

[2]Obtained from Hitachi Perkin-Elmer RMU-7L

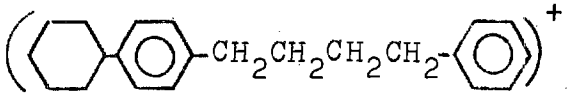
[3]Relative Abundance from Hitachi Perkin-Elmer RMU-7L

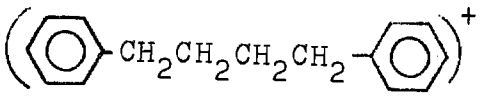
Experimental Conditions: electron energy, 80 eV; electron current, 80 uA

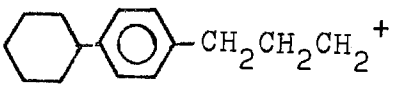
[4]Relative abundance from Varian M-66

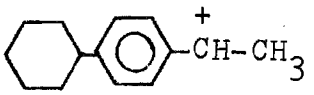
Experimental conditions: electron energy, 70 eV; electron current, 20 uA; pressure, 1 x 10^{-5} torr; analyzer temp. 150°, probe temp., 120°

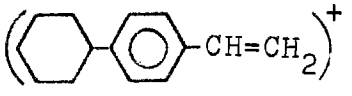
[5]Structural assignment*

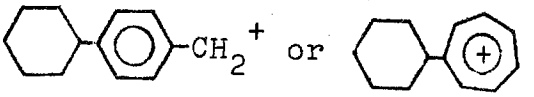
a. 

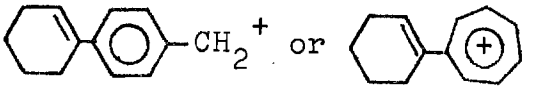
b. 

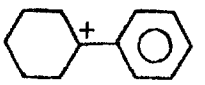
c. 

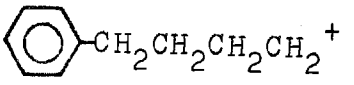
d. 

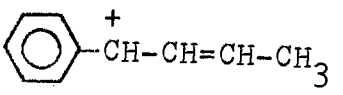
e. 

f. 

g. 

h. 

i. 

j. 

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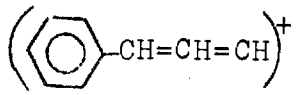
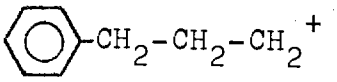
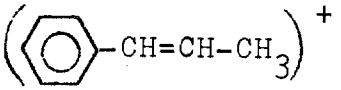
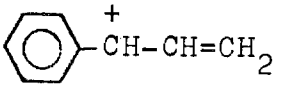
45. L. A. Konig, J. H. E. Mattauch, and A. H. Wapstra Nucl. Phys., 31, 18 (1962).

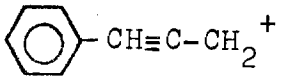
1. Compound A (Continued)

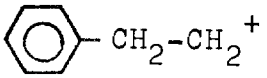
k. 

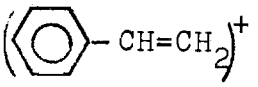
l. 

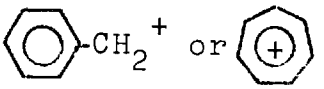
m. 

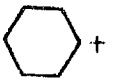
n. 

o. 

p. 

q. 

r. 

s. 

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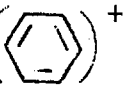
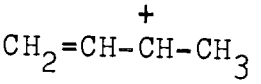
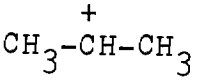
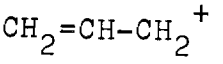
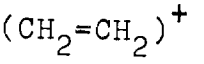
u. 

v. 

w. 

x. 

y. 

z. 

*Or related isomeric structures

2. Compound B (1-p-Cyclohexylphenyl-1,1-diphenylbutane)

Molecular formula: $C_{28}H_{32}$

Molecular weight: 368

m/e	Rel. Abund[1]	Rel. Abund[2]	Struct[3]	m/e	Rel. Abund[1]	Struct[3]
373		10		228	2	
372		34		219	3	
371		15		215	3	
370		34		205	2.5	
369		38		203	3	
368	2.5	100.0	a	202	3	
367		18		193	2	
365		25		191	5	
364		10		189	2.5	
331	2			180	1.5	
329	2.5			179	4	
327	3.5			178	6	
326	27		b	169	1.5	
325	100.0		c	168	3.5	
324	2			167	24	e
323	5			166	7	
319	2			165	30	f
269	5			153	2	
256	2.5			152	5	g
255	1.5			151	2	
253	2			149	2.5	
252	1.5			141	3	
249	3			139	1.5	
248	6.5			137	1.5	
243	2.5		d	135	1.5	
241	5			133	1.5	
239	3			131	2	

2. Compound B (Continued)

m/e	Rel. Abund[1]	Struct[3]	m/e	Rel. Abund[1]	Struct[5]
129	4	h	79	5	p
128	4		78	2	
127	3		77	6	q
121	2		71	6.5	
119	2	i	70	2.5	
117	4	j	69	11.5	
116	2		68	2.5	
115	6	k	67	6.5	
111	3.5		65	2	
110	1.5		58	5	
109	5		57	18	r
107	2.5		56	5	
105	5	l	55	24	s
104	1.5		54	2	
103	3.5		53	4	
97	5		51	2	
96	2		45	2.5	
95	5		44	5	
93	2.5		43	36	t
92	2		42	4.5	
91	19	m	41	22.5	u
85	4		39	6	
84	4		29	8.5	v
83	11	n	28	4	w
82	3		27	6	
81	7.5	o			

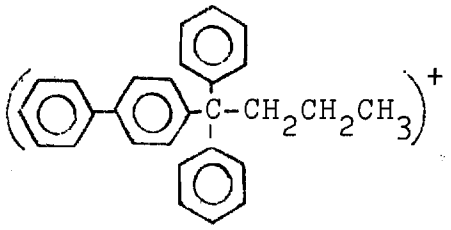
2. Compound B (Continued)

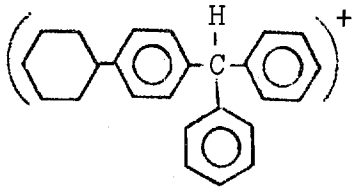
[1]Relative abundance from Varian M-66

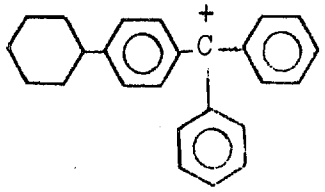
Experimental conditions: electron energy, 70 eV; electron current, 20 uA; pressure, 3.5 x 10^{-7} torr; analyzer temp., 150°; probe temp., 120°.

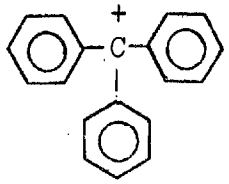
[2]Relative abundance near parent ion

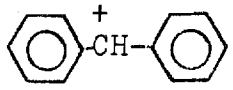
[3]Structural assignment*

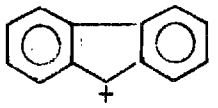
a. 

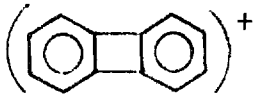
b. 

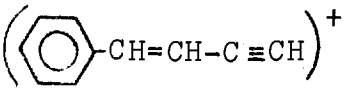
c. 

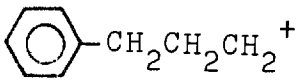
d. 

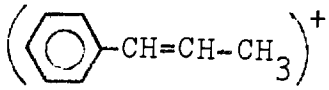
e. 

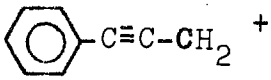
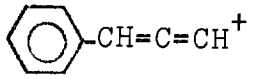
f. 

g. 

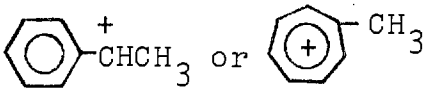
h. 

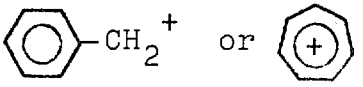
i. 

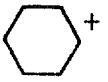
j. 

k.  or 

2. Compound B (Continued)

l.  or

m.  or

n. 

o. 

p. 

q. 

r. $CH_3CH_2\overset{+}{C}H-CH_3$

s. $CH_2=CH-\overset{+}{C}H-CH_3$

t. $CH_3-\overset{+}{C}H-CH_3$

u. $CH_2=CH-CH_2^+$

v. $CH_3-CH_2^+$

w. $(CH_2=CH_2)^+$

*Or related isomeric structures

3. Compound C (4-p-Cyclohexylphenyl-1,1-diphenylbutane)

Molecular Formula: $C_{28}H_{32}$

Exact Mass: Calcd., 368.2504;[1] obs., 368.2506[2]

m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]	m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]
373	2			182	1		
372	2.6	1.2		181	4	2.2	
371	0.7			180	18.8	8	g
370	5.5	1.2		179	1.3	1.5	
369	9	3.4		178	2.3	1.8	
368	36	12.5	a	175	2.3	1	
367	6	1.5		174	1.4	0.7	
366	14.5	5		173	8.8	5.3	h
365	0.5			172	5.5	2.5	
364	0.8			171	21.8	13.4	i
207	1.2	0.8		170	2		
206	2	0.5		169	3	4	
205	1	0.5		168	51	26.5	j
201	3	0.5	b	167	100.0	100.0	k
200	2.5	0.5	c	166	12.8	8	
199	3.0	0.5	d	165	28.4	17	l
198	1			164	1		
197	1			159	1.8	1.8	m
195	1			158	1		
194	3.5	2		157	5.5	2.5	n
193	16	6.3	e	156	0.8		
187	2	1		155	2.3	0.8	
186	13.5	5.8	f	154	0.7		
185	3.5	1		153	3	1.5	
184	0.6			152	18	8.4	o
183	0.8			151	0.8	1.3	

3. Compound C (Continued)

m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]	m/e	Rel. Abund[3]	Rel. Abund[4]	Struct[5]
145	2.2			92	4	3	
144	1			91	42	33.5	u
143	6	2.5		84	1		
142	2.6	1		83	6.2	5.2	w
141	2.8	2.2		82	1		
140	1			81	5.8	4	x
139	0.8			80	0.8		
132	2	0.8		79	3	2.2	y
131	12	7.2	p	78	2	1.6	
129	12	7.8	q	77	3.3	4.2	z
128	6.8	4.5		69	3.2	2	
127	1	1.2		67	3	3.3	
119	1.2	0.8		65	1	2.3	
118	2.8	2		57	0.5	2.3	
117	19.5	11	r	55	12	7.8	a'
116	3.3	2		53	0.6	1.8	
115	10.8	7.2	s	51	0.5	1	
108	1.3			45	0.5	1	
106	2	0.7		44	2.7	7.2	b'
105	3.7	4.8	t	43	5.6	5	c'
104	10.2	9.6	u	42	0.5	0.7	
103	5.3	4		41	3.3	6.4	d'
102	1.3	0.8		39	0.5	2	
101	1			29	1	2.7	e'
94		3.6		28	1	7.8	f'
93	2	1		27		1.6	

3. Compound C (Continued)

[1]Atomic weights:[45] C^{12}, 12.000000; H^{1}, 1.007825

[2]Obtained from Hitachi Perkin-Elmer RMU-7L

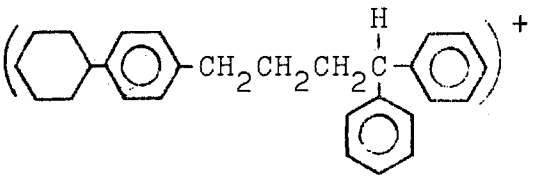
[3]Relative abundance from Hitachi Perkin-Elmer RMU-7L

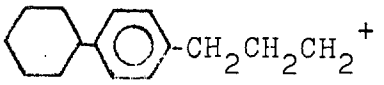
Experimental conditions: electron energy, 80 eV; electron current, 80 uA.

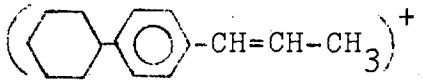
[4]Relative abundance from Varian M-66

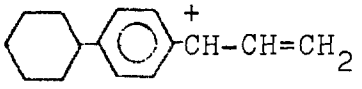
Experimental conditions: electron energy, 70 eV; electron current, 20 uA; pressure, 6 x 10^{-6} torr; analyzer temp. 150°; probe temp. 70°

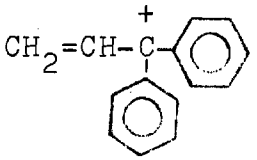
[5]Structural assignment*

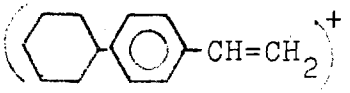
a. 

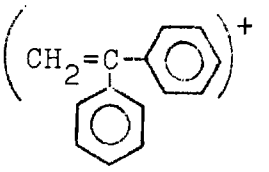
b. 

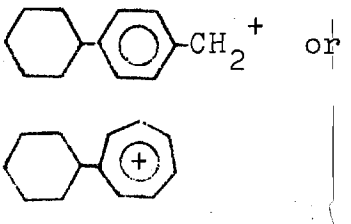
c. 

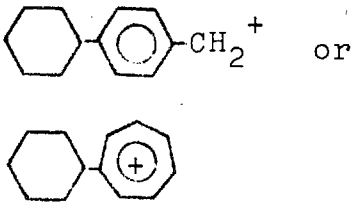
d. 

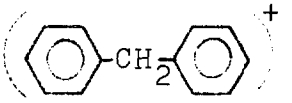
e. 

f. 

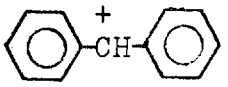
g. 

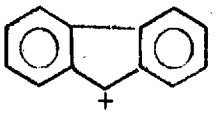
h. 

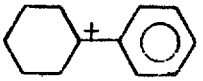
i. 

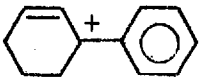
j. 

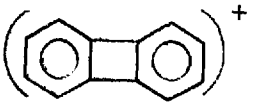
3. Compound C (Continued)

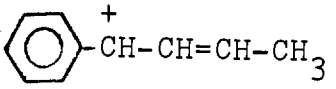
k. 

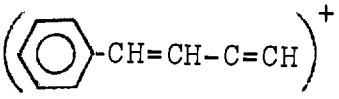
l. 

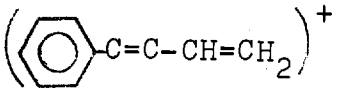
m. 

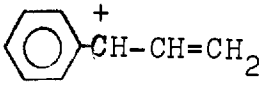
n. 

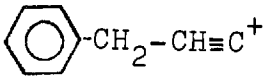
o. 

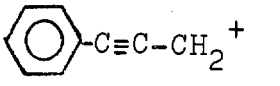
p. 

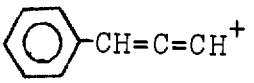
q.  or

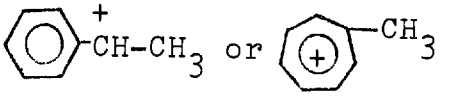


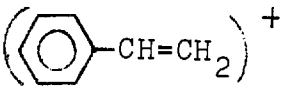
r. 

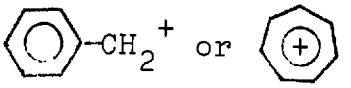
s.  or

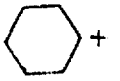
 or



t. 

u. 

v. 

w. 

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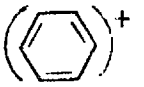
y. 

z. 

a'. $CH_2=CH-\overset{+}{C}H-CH_3$

b'. $(CH_3-CH_2-CH_3)^+$

c'. $CH_3-\overset{+}{C}H-CH_3$

d'. $CH_2=CH-CH_2^+$

e'. $CH_3-CH_2^+$

f'. $(CH_2=CH_2)^+$

4. Compound D (p-Cyclohexyldiphenylmethane)

Molecular formula: $C_{19}H_{22}$

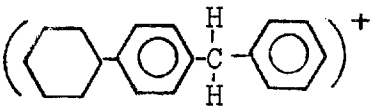
Molecular weight: 250

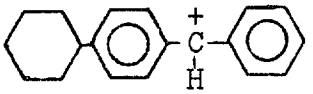
m/e	Rel. Abund[1]	Struct[2]	m/e	Rel. Abund[1]	Struct[2]	m/e	Rel. Abund[1]	Struct[2]
250	23	a	152	10	e	80	3	
249	100	b	92	6		79	6	i
168	2		91	44	f	78	7	
167	22	c	89	3		77	10	j
166	9		88	8	g			
165	25	d	81	8	h			

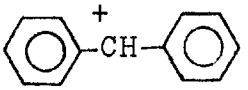
[1]Relative abundance from Varian M-66

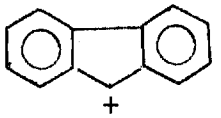
Experimental conditions: electron energy, 70 eV; electron current, 20 uA; pressure, 1 x 10^{-6} torr; analyzer temp., 150°; probe temp., 50°

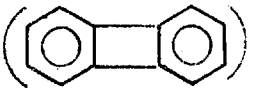
[2]Structural assignment*

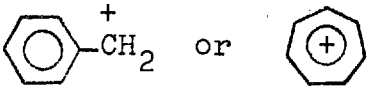
a. 

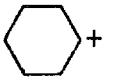
b. 

c. 

d. 

e. 

f. 

g. 

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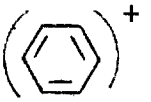
j. 

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1. A portion of this research has now been published; see E. Grovenstein, Jr., S. Akabori, and Jung-Ung Rhee, J. Amer. Chem. Soc., 94, 4734 (1972).

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VITA

Jung-Ung Rhee was born November 22, 1940, in Sung-joo, Kyung-Buk, Republic of Korea. He attended primary junior high school until his graduation from Sung-joo Junior High School in March, 1956. He entered Kyung-Buk High School in March of 1956 and graduated in February of 1959. In April of 1960, he entered the College of Liberal Arts and Sciences of Seoul National University. As a sophomore in 1961, he was drafted into the Korean Army and served as Infantry Corporal until his release in 1963. In 1963, he returned to Seoul National University as a sophomore and graduated with a B. S. Degree in Chemistry in February, 1966. He came to the United States and entered the Graduate School of the Georgia Institute of Technology in September of 1967 and completed the requirements for the degree of the Doctor of Philosophy in Chemistry in March, 1973.

On December 27, 1969, he married the former Hee-Soon Kim of Seoul, Korea.